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THE MEDICAL STUDENT'S MANUAL OF CHEMISTRY

BY

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Sixth Edition

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PREFACE TO THE PRESENT EDITION.

IN the present edition the section on chemical physics and general chemistry has been entirely rewritten so far as it applies to the former branch of the subject, and has been rearranged and extended with regard to the latter. These extensions have been necessary to permit of proper consideration of the important collateral evidence upon chemical questions which has been supplied by physical investigations, and which now constitutes so important a part of the foundation of chemical principles.

The section on inorganic chemistry, which had been condensed to the minimum in the last edition, has been almost bodily transcribed therefrom. The main purpose of this section is to supply certain data which shall serve as the text upon which to discuss the general principles of chemistry. It is the opinion of the author that the object of chemical teaching (except to advanced students in the specialties) should not be to lay up in the memory of the student a store of isolated facts, but rather to train his mind in those general principles by which he may reason out chemical problems for himself. If a teacher of chemistry to medical students aim merely to supply them with chemical facts, he and they are fore-ordained to disappointment, but if the student be led to "think chemistry," the success and possible extent of the teaching, both in the fundamentals and in the superstructure of organic and physiological chemistry, which can be attained, will be surprising and delightful to both instructor and pupil. And in this connection it must be said that the order of consideration of the several subjects which has been here followed, because it is logical, is not recommended in the teaching of students. The study should begin with that of a few elements and compounds, the consideration of the general physical and chemical principles being taken up as material for their discussion is supplied. The manner of such arrangement must be left to the judgment of the instructor.

The section on organic chemistry has been rearranged in the light of further information upon the relationships of substances,

(iii)

and somewhat extended. The prominence given to this branch of the subject the author believes to be justified, notwithstanding its intricacy and the impossibility of teaching it satisfactorily to those not well grounded in general chemistry, because of the intimate connection of organic chemistry with physiology and with modern pharmacy, and the impossibility of the comprehension of the problems of animal and pharmaceutical chemistry without the possession of an adequate knowledge of the principles of organic chemistry. In this section is included that portion of physiological chemistry treating of the properties and chemical relationships of those substances whose constitution is known, which are of physiological interest, a branch of the subject which is properly within the domain of pure chemistry.

The section on physiological chemistry has been almost entirely rewritten and greatly enlarged. The pure chemistry of the substances which are here of interest, and whose constitution is known, having been considered, in their proper places in the classification, in the preceding sections, this one is devoted to the consideration of the proteins and other substances of still unknown constitution, but particularly to the composition of the tissues and fluids of the body and the chemical processes occurring therein. This subject is one to which a vast amount of study is now being devoted, and necessarily there are many questions still under discussion and undetermined. These have been either passed over in silence or briefly referred to as undetermined, to avoid the necessity of future revision of the student's information.

It may appear to some that an apology is in order for the extent to which this book has grown. The only one which the author has to offer is that he has endeavored to keep pace with the growth of the subject, and of its appreciation by the medical profession. Nothing has been discussed which cannot and should not be taught to medical students, and, although no part of what is herein contained should be omitted in the proper training of an intended physician of the present day, the question of how much of it it should be the province of the medical school to supply is debatable, but not here. The whole can be, and is, covered in two years.

R. A. W.

NEW YORK, August, 1906.

PREFACE TO THE FIRST EDITION.

IN venturing to add another to the already long list of chemical text-books, the author trusts that he may find some apology in this, that the work is intended solely for the use of a class of students whose needs in the study of this science are peculiar.

While the main foundations of chemical science—the philosophy of chemistry—must be taught to and studied by all classes of students alike, the subsequent development of the study in its details must be moulded to suit the purposes to which the student will subsequently put his knowledge. And particularly in the case of medical students, in our present defective methods of medical teaching, should the subject be confined as closely as may be to the general truths of chemistry and its applications to medical science.

In the preparation of this Manual the author has striven to produce a work which should contain as much as possible of those portions of special chemistry which are of direct interest to the medical practitioner, and at the same time to exclude, so far as possible, without detriment to a proper understanding of the subject, those portions which are of purely technological interest. The descriptions of processes of manufacture are, therefore, made very brief, while chemical physiology and the chemistry of hygiene, therapeutics and toxicology have been dwelt upon.

The work has been divided into three parts. In the first part the principles of chemical science are treated of, as well as so much of chemical physics as is absolutely requisite to a proper understanding of that which follows. A more extended study of physics is purposely avoided, that subject being, in the opinion of the author, rather within the domain of physiology than of chemistry.

The second part treats of special chemistry, and in this certain departures from the methods usually followed in chemical text-books are to be noted. The elements are classed, not in metals and metal-loids—a classification as arbitrary as unscientific—but into classes and groups according to their *chemical* characters.

In the text the formula of a substance is used in most instances

in place of its name, *after it has been described*, with a view to giving the student that familiarity with the notation which can only be obtained by continued use.

In the third part those operations and manipulations which will be of utility to the student and physician are briefly described, not with the expectation that these directions can take the place of actual experience in the laboratory, but merely as an outline sketch in aid thereto.

Although the Manual puts forth no claim as a work upon analytical chemistry, we have endeavored to bring that branch of the subject rather into the foreground so far as it is applicable to medical chemistry. The qualitative characters of each element are given under the appropriate heading, and in the third part a systematic scheme for the examination of urinary calculi is given. Quantitative methods of interest to the physician are also described in their appropriate places. In this connection the author would not be understood as saying that the methods recommended are in all instances the best known, but simply that they are the best adapted to the limited facilities of the physician.

The author would have preferred to omit all mention of Troy and Apothecaries' weight, but in deference to the opinions of those venerable practitioners who have survived their student days by half a century, those weights have been introduced in brackets after the Metric, as the values of degrees Fahrenheit have been made to follow those Centigrade.

R. A. W.

BUFFALO, N. Y., September 16, 1883.

TABLE OF CONTENTS.

	PAGE
CHEMICAL PHYSICS—GENERAL CHEMISTRY	1
Time—Space—Matter—Force—Chemistry	1-3
General Properties of Matter :	
Indestructibility—Impenetrability—Divisibility—Inertia—Motion— Mass and Weight—Gravity—Apparent Weight—Momentum— Measure of Force—Work—Energy—Density—Specific Weight— States of Matter—Cohesion	3-13
Special Properties of Solids, Liquids and Gases	13
Crystallization—Allotropy—Diffusion—Boyle-Mariotte Law—Mixture of Gases—Absorption of Gases	13-21
Physical Actions of Chemical Interest	21
HEAT:	
Temperature—Thermometers—Thermal Unit—Changes in Volume— Dalton - GayLussac Law—Absolute Temperature—General Gas Law—Dynamic Theory of Heat—Kinetic Theory of Gases— Change of State—Fusion—Heat of Fusion—Solution—Vaporiza- tion—Gases and Vapors—Equilibrium—Boiling—Sublimation— Heat of Vaporization—Specific Heat	21-33
LIGHT:	
Index of Refraction—Spectroscopy—Polarimetry—Chemical Effects of Light	34-39
ELECTRICITY:	
Insulators—Conductors—Ions—Galvanic Electricity—Electromotive Force—Quantity—Resistance—Ohm's Law—Current Density— Divided Currents—Electrolysis—Polarization—Electrical Units— Resistance and Conductance—Electromotive Force—Work— Heat—Power	39-46
Chemical Phenomena	47
Elements—Non-elementary Substances—Compounds—Physical Mix- tures—Molecular and Atomic Theories—Atomic Weight—Mo- lecular Weight—Mol—Molecular Volume—Molecular Heat— Valence—Symbols, Formulæ and Equations—Electrolysis—Acids, Bases and Salts—Concentration—Osmotic Pressure—Electrolytic Dissociation—Stoichiometry—Nomenclature—Radicals—Com- position and Constitution—Chemical Energy—Chemical Equi- librium—Reversible Reactions—Velocity of Reaction—Mass Action—Phase Rule—Thermochemistry—Classification of Ele- ments—Periodic Law	47-104

	PAGE
INORGANIC CHEMISTRY	105
Typical Elements	105
Hydrogen	105
Oxygen	109
Compounds of Hydrogen and Oxygen: Water—Natural Waters—	
Hydrogen Peroxid	113-124
Elements which form no Compounds	125
Helium—Neon—Argon—Krypton—Xenon	125
Acidulous Elements	125
CHLORIN GROUP	125
Fluorin	126
Chlorin	127
Compounds of Chlorin	130-133
Bromin	133
Compounds of Bromin	134-135
Iodin	135
Compounds of Iodin	136-137
SULFUR GROUP	138
Sulfur	138
Compounds of Sulfur	139-147
Selenium and Tellurium	147
NITROGEN GROUP	148
Nitrogen	148
Atmospheric Air	149
Compounds of Nitrogen	151-159
Phosphorus	159
Compounds of Phosphorus	165-169
Arsenic	169
Compounds of Arsenic	170-182
Antimony	183
Compounds of Antimony	183-187
BORON GROUP	187
Boron and its Compounds	187
CARBON GROUP	188
Carbon	188
Silicon and its Compounds	190-191
VANADIUM GROUP	191
Vanadium—Niobium—Tantalum	191-192
MOLYBDENUM GROUP	192
Molybdenum—Tungsten—Osmium	192
Amphoteric Elements	193
GOLD GROUP	193
Gold and its Compounds	193-194
IRON GROUP	194
Chromium and its Compounds	194-195
Manganese and its Compounds	195-197
Iron and its Compounds	197-203

TABLE OF CONTENTS

ix

	PAGE
URANIUM GROUP	203
Uranium and its Compounds	203
LEAD GROUP	204
Lead and its Compounds	204-208
BISMUTH GROUP	209
Bismuth and its Compounds	209-211
TIN GROUP	211
Titanium	211
Zirconium	211
Tin and its Compounds	212-213
PLATINUM GROUP	213
Palladium — Platinum	213-214
RHODIUM GROUP	213
Rhodium — Ruthenium — Iridium	213
Basilous Elements	215
SODIUM GROUP	215
Lithium and its Compounds	215-216
Sodium and its Compounds	216-221
Potassium and its Compounds	222-230
Cesium — Rubidium	230
Silver and its Compounds	230-232
Ammonium Compounds	232-234
THALLIUM GROUP	235
Thallium	235
CALCIUM GROUP	235
Calcium and its Compounds	235-238
Strontium and its Compounds	238-239
Barium and its Compounds	239-240
MAGNESIUM GROUP	240
Magnesium and its Compounds	240-242
Zinc and its Compounds	242-245
Cadmium	245
ALUMINIUM GROUP	245
Beryllium — Scandium — Gallium — Indium	245
Aluminium and its Compounds	245-248
NICKEL GROUP	249
Nickel	249
Cobalt	249
COPPER GROUP	250
Copper and its Compounds	250-254
Mercury and its Compounds	254-261
ORGANIC CHEMISTRY	262
Compounds of Carbon :	
Homologous Series — Isomerism — Elementary Organic Analysis — De-	
termination of Molecular Weights — Determination of Constitu-	
tion — Nomenclature — Classification of Organic Compounds . . 262-272	

	PAGE
Open Chain, Aliphatic, Acyclic, or Fatty Compounds	272
HYDROCARBONS	272
SATURATED COMPOUNDS—METHANE SERIES	272
Hydrocarbons	272-277
Haloid Derivatives	277-282
Oxidation Products	282
Alcohols	284-298
Aldehydes and Ketones	298-308
Aldehyde-alcohols—Ketone-alcohols—Aldehyde-ketones and Oxy- aldehyde-ketones	308
Carbohydrates	309-327
Carboxylic Acids	327-338
Alcohol-acids—Oxyacids	338-346
Aldehyde-acids	346
Ketone-acids	347-348
Oxaldehyde and Oxyketone Acids	348
Simple Ethers	348-351
Acid Anhydrides	351-358
Esters—Compound Ethers	358-370
Sulfur Derivatives of the Paraffins	370-375
Organo-metallic Compounds	375-376
Nitrogen Derivatives of the Paraffins	376
Nitroparaffins	376-377
Amins and Ammonium Derivatives	377-382
Oxyamins—Hydramins—Diamins—Imins—Diimins	382-388
Amidins—Amidoxims—Hydroxamic Acids	388
Guanidin and its Derivatives	388-390
Hydrazins—Hydrazids	390
Nitrils—Cyanogen Compounds	391-399
Amids	399-405
Thiourea and Thiocarbamic Acid	405-406
Compound Ureas	406-408
Nitrogen Derivatives of Alcohols, Aldehydes and Ketones	408-410
Nitrogen Derivatives of Acids	410-422
Phosphorus, Antimony and Arsenic Derivatives	422-423
UNSATURATED ALIPHATIC COMPOUNDS	423
Hydrocarbons	423-426
Halogen Derivatives	426
Oxidation Products	426-431
Sulfur and Nitrogen Compounds	432
Closed Chain Compounds—Cyclic Compounds	433
CARBOCYCLIC COMPOUNDS	434
HEXACARBOCYCLIC COMPOUNDS—AROMATIC SUBSTANCES	435
Monobenzenic Compounds	440
Hydrocarbons	440-442
Haloid derivatives	442
Phenols	443-451
Quinones	451
Aromatic alcohols	452

TABLE OF CONTENTS

xi

	PAGE
Alphenols	453
Aldehydes	453
Ketones	455
Aromatic Carboxylic Acids	455-464
Phenylic Ethers—Glucosids	464-468
Anyhydrids and Acid Halids	468
Aromatic Sulfur Derivatives—Sulfonic Acids	469
Nitrogen-containing Derivatives of Benzene	470-486
HYDROAROMATIC COMPOUNDS	486
Hydrocarbons	486-489
Hydroaromatic Alcohols	489-491
Hydroaromatic Ketones and Acids	491-493
COMPOUNDS WITH CONDENSED NUCLEI	493
Condensed Hydrocarbons	494-496
Haloid Derivatives—Orientation	495
Phenols—Alcohols—Aldehydes—Ketones—Quinones—Carboxylic Acids	497-500
Nitrogen Derivatives	500
DIPHENYL AND ITS DERIVATIVES	501
DIPHENYL-PARAFFINS—DIPHENYL-OLEFINS—DIPHENYL-ACETYLENES	502
Phenols—Alcohols—Ketones and Carboxylic Derivatives	503
Nitrogen-containing Derivatives	504-506
HETEROCYCLIC COMPOUNDS	507
MONONUCLEATE HETEROCYCLIC COMPOUNDS	509
Five-membered rings	509-516
Six-membered rings	516-537
CONDENSED HETEROCYCLIC COMPOUNDS	537
Condensed Nuclei Containing Oxygen or Sulfur Members	539
Condensed Nuclei Containing a Nitrogen Member	539-544
PHENYL-PYRIDYL—DIPYRIDYL AND PYRIDYL-PYRROLE COMPOUNDS	545
Alkaloids	545-570
Ptomaines, Leucomaines and Toxins	570-573
PHYSIOLOGICAL CHEMISTRY	574
PROTEINS	575
Native Albumins	583-591
Proteids	591-595
Albuminoids	595-597
CHEMICO-PHYSIOLOGICAL PROCESSES	597
Ferments and Enzymes	599-606
DIGESTION	606
Saliva	606-608
Gastric Juice and Gastric Digestion	608-625
Pancreatic Secretion and Digestion	626-631
Intestinal Secretions	632
The Bile	633-642
Chemical Changes in the Intestine	642-649

	PAGE
THE BLOOD	649
Plasma and Serum	650-656
Blood Corpuseles	656-667
The Blood as a Whole	667-669
Blood Serum and Bacterial Action	669-675
Physico-chemical Examination of Blood	675-677
Changes in Composition of the Blood in Different Parts of the Circulation	677-692
LYMPH—CHYLE—TRANSUDATES—EXUDATES	692-694
URINE	694
Physical Characters	694-699
Normal Mineral Constituents	699-706
Normal Organic Constituents	706-733
Abnormal Constituents	733-758
URINARY CALCULI	758-761
MILK	761-767
APPENDIX	769-781
INDEX	783

SIGNS AND ABBREVIATIONS.

The figures in parentheses indicate the page upon which the meaning of the sign or abbreviation is described.

Aq	=Water of crystallization (116).	a	=Coefficient of expansion of gases.
C	=Current strength (41).	[a] _D	=Specific rotary power for sodium light (38).
C	=Component (97).	atm	=Atmospheric pressure (8).
C*	=Asymmetric carbon atom (313).	b. p.	=Boiling point (32).
C.G.S.	=Centimeter:gram:second (6, 7).	cal.	=Gram calorie (20).
D	=Density (9).	cc	=Cubic centimeter (1).
E	=Electromotive force (40).	c.c.	=Cubic centimeter.
EMF	=Electromotive force (40).	c ³	=Cubic centimeter.
F	=Faraday (72).	cm ³	=Cubic centimeter.
F	=Degree of freedom (94).	cm	=Centimeter (1).
H.P.	=Horse power (8).	cm ²	=Square centimeter (7).
K	=Rational calorie (20).	d	=Dextrogyrous (311, 313).
L	=Liter (2).	d+l	=Racemic (311, 313).
M	=Molecule (53).	dm	=Decimeter (1).
N	=Normal (65).	f. p.	=Fusing point (26).
N/10	=Tenth normal, etc.	gm	=Gram (6, 779).
ND ₁₀₀	=Normal current density (43).	i	=Racemic (311, 313).
P	=Weight (9).	i	=Iso (274).
P	=Phase (93).	k	=Velocity constant (91).
R	=Resistance (41).	kg	=Kilogram (779).
R	=A cyclic compound (434).	kg:cal	=Large calorie (20).
SS	=Standard solution (65).	kg:m	=Kilogram:meter (8).
T	=Absolute temperature (21).	km	=Kilometer (1, 778).
V	=Volume (9).	l	=Lævoggyrous (311, 313).
V _m	=Molecular volume (58).	m	=Meter (1).
V _s	=Specific volume (9).	m	=Meta (438).
A	=Ampère (43).	mm	=Millimeter (1).
C	=Asymmetric carbon atom (313).	n	=Index of refraction (34).
C	=Coulomb (43).	[n] _D	=Index of refraction for sodium light (34).
F	=Force (7).	o	=Ortho (438).
J	=Joule's equivalent (20).	p	=Weight (8).
K	=Dissociation constant (75).	p	=Para (438).
K	=Kinetic energy (8).	p/m	=Per thousand.
Kj	=Kilojoule (20).	ppt.	=Precipitate.
Kw	=Kilowatt (44).	r	=Racemic (311, 313).
M _w	=Molecular weight (56).	sec	=Mean solar second (1, 7).
P	=Pressure.	sp. gr.	=Specific gravity (8).
T	=Cryoscopic constant (68).	t	=Temperature in degrees Centigrad.
V	=Volt (43).	t	=Variation of temperature (68).
V	=Mean velocity (5).		
W	=Work (8).		
W	=Watt (44).		
Wj	=Joule (8).		

v	=Volume (8).	Δ	=Double linkage (57).
a	=Acceleration (4).	Δ	=Depression of freezing point (5).
c_p	=Specific heat at constant pressure (33).	Δ	=Equivalent conductivity (75).
c_v	=Specific heat at constant volume (32).	γ	=Dissociated fraction (74).
g	=Acceleration of gravity (6).	v	=Concentration in grams per cubic centimeter (74).
i	=Van't Hoff's factor (74).	κ	=Specific conductivity (41).
l	=Length, space, distance (4).	λ	=Wave length of light (36).
m	=Mass (5).	μ	=Molecular conductivity (74).
mc	=Momentum (7).	μ	=Micromillimeter = .001 millimeter.
p	=Pressure.	+	=Dextrogyrous (311, 313).
t	=Time.	-	=Larogyrous (311, 313).
v	=Velocity.		
Δ	=Mean difference (76).		

THE MEDICAL STUDENT'S MANUAL OF CHEMISTRY.

CHEMICAL PHYSICS—GENERAL CHEMISTRY.

Time and Space.—In the study of the phenomena affecting material objects we have to do with the elementary concepts of time and space, only in so far as we have occasion to measure those fractions thereof which come within human comprehension.

The unit of time-measure is the **mean solar day**, which is the average duration of the intervals between 366 successive meridional transits of the sun, i. e., apparent days. This average is taken because apparent days are not exactly equal to each other. For physical and chemical investigations this unit is too large, and the fraction which is used is the **mean solar second** (sec.) $\frac{1}{86400}$ of the mean solar day.

Space, or that fraction thereof of which we have knowledge, may be said to be the interval between any two or more locations. The unit of measure of space in one dimension, **length**, is the distance, at the temperature of melting ice, between two lines upon a bar of platiniridium preserved near Sèvres, in France; many accurate copies of which are also preserved in other places. It is the fundamental unit of the entire system of metric measures, weights and coinage, and of numerous scientific units, and is called the **meter** (m.). It was intended to be $\frac{1}{10000000}$ of the earth's meridional circumference, from which it varies very slightly. It is equal to 39.37079 inches. This unit is subdivided decimally, and its fractions are indicated by the Latin numerals: the meter contains 10 **decimeters** (dm.), 100 **centimeters** (cm.), and 1000 **millimeters** (mm.) (as the dollar contains 10 dimes, 100 cents, and 1000 mills). The multiples of the meter are designated by the Greek numerals: 10 meters=1 **decameter**, 100 meters=1 **hectometer**, and 1000 meters=1 **kilometer**.

The measures of space in two dimensions, **area**, are the squares of the measures of length; and the measures of space in three dimensions, **volume**, are their cubes. A cubic decimeter is called a liter

(L), which contains 1000 cubic centimeters (cc., or c.c., or c.³, or cm.³).

Matter and Force.—As we only become cognizant of matter by the action of force upon it, or of force through its effects upon matter, our appreciations of each are so interwoven that each is usually defined in terms of the other. This "argument in a circle" may be avoided by saying that **matter is that which occupies space**. A given space may be occupied by widely varying amounts of matter, from the trace of highly tenuous vapor in a barometric vacuum to the most compact metal. Even the interplanetary spaces, as well as the spaces between the molecules (p. 4) of material substances, are filled with the **luminiferous ether**, which, although extremely subtile, must be considered to be material. The amount of matter in unit space determines its **concentration** (p. 64). If this amount be relatively large the form in which the matter exists, gas, solution, etc., is said to be **concentrated**, if relatively small it is said to be **dilute**.

In popular language the words "matter" and "substance" are used synonymously; but in chemical language the latter word has a more narrow meaning. A **substance** is a species of matter, having constant characters and properties by which it may be recognized, and differentiated from other substance species, irrespective of its shape. Thus sulphur, water, chalk are chemical substances, each of which, in any form in which it may appear, has definite qualities by which it may be distinguished from all other species of substance.

Force is that which produces, or tends to produce motion, or change of motion of matter.

Different species of force differ in the character of the motion which they produce, and in the magnitude of the quantities of matter upon which they act; from gravitation, which acts upon all bodies, even to the greatest, to chemical force, which acts upon the most minute particles, the atoms (p. 53). Light, heat, sound, electricity, mechanical motion are other species of force. These several species are convertible one into the other in certain definite quantitative relations; as when mechanical force is transformed into heat, electricity, light, etc. (pp. 9, 22).

Chemistry.—The simplest definition of chemistry is a modification of that given by Webster: **That branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes.**

A bar of soft iron may be made to emit light when heated, or sound when caused to vibrate, or magnetism when under the influence of an electric current. Under the influence of these **physical forces** the iron suffers no change in composition, and, on cessation of the action of the inciting force the iron returns to its original

condition. But if the iron be heated in an atmosphere of oxygen, both the iron and a part of the oxygen disappear, and a new substance, a new chemical species, is produced, having properties of its own, different from those of either the iron or the oxygen. In this case there has been **chemical action**, causing change of composition, as the new substance contains both iron and oxygen. The result of such action is, moreover, permanent, and the new product continues to exist, until modified by some new manifestation of chemical action.

While chemical action is thus different in its results from the actions of physical forces, there exists the most intimate relation between them. As above stated, they are interconvertible. The line of demarcation between chemical actions and certain physical actions, such as solution, although distinct, is narrow. Many chemical actions take place only under certain physical conditions, such as of temperature; or are provoked by physical forces, such as light. Indeed, the entire structure of theoretical or general chemistry has among its most secure foundations results obtained in the study of **chemical physics**, which is, therefore, a most important collateral branch of chemistry as well as of physics.

GENERAL PROPERTIES OF MATTER.

Indestructibility.—The result of chemical action is change in the composition of the substance acted upon, a change accompanied by corresponding alterations in its properties. Although we may cause matter to assume a variety of different forms, and render it, for the time being, invisible, yet in none of these changes is there the smallest particle of matter destroyed. When carbon is burned in an atmosphere of oxygen, it disappears, and, so far as we can learn by the senses of sight or touch, is lost; but the result of the burning is an invisible gas, whose weight is equal to that of the carbon which has disappeared, plus the weight of the oxygen required to burn it.

Impenetrability.—Although one mass of matter may penetrate another, as when a nail is driven into wood, or when salt is dissolved in water, the ultimate particles of which matter is composed cannot penetrate each other, and, in cases like those above cited, the particles of the softer substance are forced aside, or the particles of one substance occupy spaces between the particles of the other. Such spaces exist between the ultimate particles of even the densest substances.

Divisibility.—All substances are capable of being separated by mechanical means into minute particles. Although we have no direct experimental evidence of a limit to this divisibility, we are warranted in believing that matter is not infinitely divisible. A strong argu-

ment in favor of this view is that, after physical subdivision has reached the limit of its power with compound substances, these may be further subdivided into smaller, dissimilar quantities by chemical means. The limit of physical subdivision of matter is the **molecule** of the physicist, the smallest quantity of matter with which he has to deal, the smallest quantity that is capable of free existence (pp. 52, 56).

Inertia—is that negative quality of matter by virtue of which it cannot of itself produce any change in the condition of rest or of motion in which it may be. If matter be at rest it can only be put in motion by the expenditure of work upon it, and, if it be in motion, such motion will continue, rectilinear, uniform, and indefinite, unless interfered with by the interposition of other energy (p. 7).

Motion.—A **material particle** is a body of such small *relative* magnitude that it may be considered as being concentrated in a point. The earth, in its relations to the solar system, is a material particle, while in its relation to smaller objects near its surface it is a body of enormously preponderating magnitude.

The **absolute position** of a particle in space cannot be fixed, but its **relative position**, usually referred to as its *position* may be fixed by three arbitrary coördinates, x, y, z ; as the position of the balloon may be located by its latitude, longitude, and elevation above the sea-level.

Motion or displacement of a particle is a change in its position. The **velocity** (v) of motion of a particle is the rate of its change of position in a given direction, expressed in space or distance (l), and time (t): i. e., $v = \frac{l}{t}$, (I). Velocity is **uniform** when the spaces traversed in equal times are equal to each other. It is **accelerated** when such spaces are unequal; **positively** accelerated when they become greater, **negatively** accelerated when they become less. Motion is **uniformly accelerated** when the rate of change in equal times is constant.

The following are **Newton's Laws of Motion**: I. *All bodies persevere in a state of rest or in a state of uniform motion in a straight line, except in so far as they are made to change that state by the action of force.* II a. *The rate at which the velocity of a particle changes is parallel and proportional to the force acting upon the particle.* II b. *The rate at which a given force changes the velocity of a particle is inversely proportional to the mass of the particle* (see p. 5). III. *Action is equal to reaction and in a contrary direction.*

The first law is a statement of the condition of inertia, when no force is acting. But the fact that a particle is at rest does not imply that no force is acting upon it. It will remain at rest when two or

more forces are acting upon it in such manner that their algebraic sum is zero; when the forces are in equilibrium.

Any constant and uniform force, acting without interference, produces a rectilinear and uniformly accelerated motion of the particle to which it is applied, in the direction of action of the force; the amount of the acceleration being proportionate to the intensity of the force, in obedience to IIa above.

Uniformly accelerated motion obeys the following laws:

Let v represent the velocity at the end of time t , v' the initial velocity, and a the acceleration, then $a = \frac{v-v'}{t}$ or, if $v'=0$, as it does when motion begins at rest, then $a = \frac{v}{t}$, (II). That is: *The velocities are proportionate to the times*, i. e., 1, 2, 3, etc. It also follows that the acquired velocity at the end of any given number of units of time is $v = at + v'$, or, if $v'=0$; $v = at$, (III); and also that the **mean velocity** (V) is one-half of the final velocity, plus the initial velocity: $V = \frac{1}{2}at + v'$, or, if $v'=0$; $V = \frac{1}{2}at$, (IV).

As $a = \frac{v}{t}$, and $v = \frac{l}{t}$; $a = \frac{l}{t^2}$, (V). That is: *The spaces traversed are proportionate to the squares of the times*. It is clear also that the total space traversed during any given number of units of time is the same as would have been traversed with a *uniform* velocity, equal to the mean velocity of the uniformly accelerated motion, in the same number of units of time.

It may also be demonstrated that: *The spaces traversed in given times are equal to one-half of the acceleration, multiplied by the squares of the times*: $l = \frac{1}{2}at^2$, (VI).

Mass and Weight.—If we imagine a gun so mounted that its recoil may take place without friction in a vacuum, and that the velocity of the recoil and the muzzle velocity of the projectile may be accurately measured, we will find that these velocities are not equal. As here one and the same force, the explosion of the powder, produces both motions, they should be in all respects equal, in obedience to Newton's laws IIa and III (p. 4), were it not that the two bodies have different **masses**; and, in obedience to Newton's law IIb, if the velocity of the recoil be 10 feet per second, and the muzzle velocity of the projectile 1,000 feet per second, the two masses are inversely as these velocities, i. e., the mass of the projectile being 1, that of the gun is 100.

If now the projectile be a one-pound shot, the weight of the gun will be found to be 100 pounds, i. e., *the mass is proportionate to the weight*; and the mass of a body is usually determined by ascertaining its **absolute weight**, i. e., its weight in a vacuum. But mass is not weight, for if we could transfer the experiment with the gun to the

center of the earth, the ratio between the two velocities would remain the same, but neither gun nor the projectile would have any weight. Weight is a manifestation of the attraction of gravitation of the earth.

Gravity.—All material particles mutually attract each other; and the force of such attraction between two particles is directly as the product of their masses, m and m' , and inversely as the distance l , which separates them: $\frac{m \times m'}{l}$. Between three or more particles the attraction exerted upon each is the resultant of the attractions of all of the others.

A body may be considered as made up of particles, and the attraction between two bodies is the sum of all the attractions between the particles of which they are composed. These attractions may be reduced to a single resultant, exerted between two points which are the **centers of mass**, or of **inertia**, or of **gravity** of the two bodies. The **attraction of gravitation**, which the earth exerts with surrounding bodies, is, therefore, a force which is manifested as weight when not free to cause motion, and, when free to do so, produces motion of the lesser mass in a straight line toward the center of mass of the earth, and, as the force of gravity is constant and uniform, such motion is uniformly accelerated.

The force of gravity has served, by the use of Atwood's machine, for the study of uniformly accelerated motions. It has been determined that the **acceleration of gravity**, g , which varies with the altitude and the latitude, is 9.8048 meters per second at the sea-level and in latitude 45° . There a freely falling body acquires velocities of 9.8048, 19.6096, 29.4144, etc., meters per second in 1, 2, 3, etc., seconds (Eq. II, p. 5); and traverses 4.9024, 9.8048, 14.7072, etc., meters during 1, 2, 3, etc. seconds (Eq. V).

Apparent Weight.—The weight of a body as determined with our balances is not exactly the same as the absolute weight if the weights and the body weighed be not of the same size. All bodies weighed in air suffer a loss of absolute weight by the amount of the weight of the air which they displace. Therefore, if the body weighed be voluminous and light, and the weights heavy and small, the bouyant effect of the air is greater upon the former than upon the latter, and the **apparent weight** of the former is by so much less than its absolute weight. In ordinary chemical operations the difference between absolute and apparent weight is so slight that it is neglected.

In weighing, pieces of brass, platinum, aluminum or quartz, of definite mass, and referred to a standard, are used as **weights**. The unit of these weights is the **gram**, gm., which is $\frac{1}{1000}$ of the weight of a mass of platiniridium, preserved along with the standard meter (No. 1), whose weight is in turn equal to the weight of one cubic

decimeter of pure water at 4°C. The gram is, therefore, the weight of one cubic centimeter of pure water at 4°C. The fractions and multiples of the gram are designated in the same manner as those of the meter. (See Table II in the Appendix.)

Momentum.—Newton's second law of motion (p. 4) refers to what is now called momentum. The power of producing results, of doing work, of a moving body depends upon both its mass and its velocity. The product of the mass of a moving body, multiplied by its velocity is its momentum: mv , or $\frac{ml}{t}$, (VII).

Measure of Force—C. G. S. System.—The measure of force is also derived from mass and velocity. The unit of measure of force is that force which, acting upon unit mass during unit time, produces a velocity of unit distance in unit time: $F = \frac{m}{t} \times \frac{l}{t} = \frac{ml}{t^2}$, (VIII). And, as a uniformly accelerated force produces at the end of the first unit of time a velocity equal to its acceleration (p. 5), force is measured by the mass, multiplied by the acceleration: $F = ma$.

In these algebraic expressions any values may be chosen for the several quantities; the mass m may be measured in grams, kilos, pounds, etc.; the distance l in centimeters, meters, feet, etc.; and the time t in seconds, minutes or hours.

For scientific measurements the **C. G. S. system**, sometimes erroneously called the system of absolute units, has been universally adopted, and includes units for the measurement of a great variety of quantities. The system owes its name to the selection of the centimeter, cm., the gram, gm., and the second, sec., as the units respectively of distance (space in one dimension), mass and time. From these three **fundamental units** all others are derived. Thus the unit of area is the square centimeter, cm^2 , and the unit of volume is the cubic centimeter, cm^3 . The unit of momentum is the momentum of a body having a mass of one gram, moving with a velocity of one centimeter per second; i. e., $\frac{ml}{t} = \frac{\text{gm.} \times \text{cm.}}{\text{sec.}}$.

In this system the unit of force is called the **dyne**, and is that force which, acting upon a mass of one gram for one second, generates a velocity of one centimeter per second; i. e., $\frac{mv}{t} = \frac{ml}{t^2} = \frac{\text{gm.} \times \text{cm.}}{(\text{sec.})^2}$. The dyne is nearly equivalent to $0.102 = \frac{1}{9.81}$, the weight of one milligram. As a larger unit the **megadyne** = dyne $\times 10^7$, and nearly equivalent to the weight of 1.02 kilo, is used. The C. G. S. units in many cases are too small or too large for general use, and for technical purposes so-called **practical units**, having definite relations to the C. G. S. units, have been adopted.

In the **English system** the unit of force is the **poundal**, which is

that force which, acting upon a mass of one pound for one second, generates a velocity of one foot per second. It is equal to 13,825 dynes.

Work.—To cause a change in the position of a particle requires an exertion which is called **work** (p. 4). Energy is said to *do work*, therefore, whenever it initiates or arrests motion, or changes such motion, or maintains it in opposition to the effects of other work. If the distance through which a particle is moved be doubled, double the *amount* of work will be required to effect the change. The relation of work to unit force is measured by the space through which motion is effected: $W=Fl$. Or, if unit force be $F=\frac{ml}{t^2}$, (Eq. VIII, p. 7), unit work is $W=\frac{ml^2}{t^2}$, and, as $v=\frac{l}{t}$, (Eq. I); $W=mv^2$, (IX). That is, work is equal to the mass, multiplied by the square of the velocity.

The C. G. S. unit of work is the amount of work done by unit force, one dyne (p. 7), working through unit space, one centimeter, in unit time, one second, and is called the **erg**: $\text{Erg}=\frac{\text{gm.} \times \text{cm.}^2}{\text{sec.}^2}$. For most purposes the erg is inconveniently small, and a multiple thereof, 10^7 ergs, called the **joule**, W_J , is generally used. For technical uses work may also be measured in **foot-pounds**, or **kilogram-meters** (kg:m.), i. e., the work required to raise one pound through one foot, or one kilogram through one meter in opposition to gravity. One kg:m. is equal to 9.81×10^7 ergs.

The conception of work takes no account of the time in which the work is done. When this is considered the result is known as **power**, and is measured in terms of unit work done in unit time: $\frac{ml^2}{t^3}$. The C. G. S. units are one erg per second: erg:sec., and the **watt**, which is one joule per sec: W_J :sec. The technical unit is the **horse power** (H. P.), which is 550 foot-pounds per second. The French "*force de cheval*" is 75 kilogram-meters per second, and equal to 542.48 foot-pounds per second.

Energy.—As a result of the expenditure of work upon matter, the latter may be placed in a relation in which the actual performance of work ceases, but in which the matter has acquired a *position* from which it is capable of doing work. Thus, to lift a stone to the top of a wall from the ground requires the expenditure of a definite number of foot-pounds of work. Supported on the wall the stone does no work, but if allowed to fall, it can in so doing develop the same number of foot-pounds of work as were required to lift it. **Energy** includes both that exertion which is doing work, which is known as **actual** or **kinetic energy**, and that capacity to do work which is

known as **possible** or **potential** energy. The relative amounts of the two forms change constantly, but their sum is a constant quantity; i. e., *energy, like matter, can neither be created nor destroyed.*

One form or variety of energy may be converted into another, and when such conversion takes place there exist definite quantitative relations between the two forms or varieties. There is a general tendency toward the conversion of all forms and varieties of energy into the one form of heat, which in turn tends to diffuse itself uniformly throughout all matter. This tendency, which is referred to as the **degradation** or **dissipation** of energy, must lead, if continued, to a final uniform temperature throughout the universe, and the consequent cessation of all physical phenomena.

There is no general quantitative expression of potential energy, except by difference. But for kinetic energy, such an expression may be derived from comparison with a capacity to do work. As the work performed by the earth's attraction upon a freely falling body finds its expression in the increase of kinetic energy, as $W=mv^2$, and as the mean velocity of uniformly accelerated motion beginning at rest is one-half of its final velocity, the measure of kinetic energy is one-half of the product of the mass, multiplied by the square of the final velocity: $K=\frac{1}{2}mv^2$, or, in C. G. S. units: $\frac{1}{2}$ erg.

Density.—The **absolute density** of a body is the ratio between its volume and its weight, and is obtained by the formula $D=\frac{P}{V}$, in which D is the density, P the weight, and V the volume. Clearly, also $P=VD$, and $V=\frac{P}{D}$.

When V is taken as the unit of volume the equation $D=\frac{P}{V}$ becomes $D=P$; i. e., *the absolute density of a substance is the weight of unit volume of that substance.* But as the weight of a given volume of a substance, particularly in the liquid or aëriform state, varies with differences of temperature and of pressure, a definite temperature and pressure have been arbitrarily selected as constituting **normal conditions**. The temperature is 0°C., and the pressure that of a column of mercury 76 centimeters high at 45° latitude. As one liter of oxygen weighs 1.4291 grams, and one liter of hydrogen weighs 0.0900 gram under normal conditions, 1.4291 and 0.0900 are the absolute densities of oxygen and hydrogen respectively. As 1 cc. of air weighs .001293 gm. under normal conditions, the absolute density of a gas for 1 cc. may be obtained by multiplying its specific gravity, air 1 (p. 10), by .001293. Thus the specific gravity of oxygen being 1.1054, 1 cc. of oxygen weighs $1.1054 \times .001293 = .001429$ gms.

Pressures are measured either by the height of a column of mercury which the pressure will sustain in opposition to gravity, in cm.

or mm.; or in atmospheres, one atm. being the pressure which will sustain a column of mercury of the average height of the barometer; i. e., 760 mm. As the specific gravity (below) of mercury is 13.6 at 0°C., 1 cc. of mercury weighs 13.6 gms., and each mm. of mercurial column is equivalent to a pressure of 1.36 gms. per sq. cm., and one atm. of pressure is equal to 1033.6 gms. per sq. cm.

The Specific Weight, or Specific Gravity, or Relative Density of a substance is the weight of a given volume of the substance as compared with the weight of an equal volume of some substance, accepted as a standard of comparison, under like conditions of temperature and pressure. The sp. gr. of solids and liquids are referred to water, and are usually determined at 15°C. To express the sp. gr. of solids and of heavy liquids, the weight of one cc. of water is taken as the unit. Thus the sp. gr. of sulfuric acid being 1.84, 1 cc. of water weighing 1 gm., 1 cc. of sulfuric acid weighs 1.84 gms. For light liquids one liter of water is the unit. Thus 1 L. of a liquid of sp. gr. 1.026 weighs 1026 gms., or 1.026 kg. In metric, therefore, the weight of 1 cc., or of 1 L. of a liquid represents its specific gravity.

The specific gravities of aëriiform bodies are expressed in three different ways. They are usually determined with reference to pure, dry air at 0°C. and 76 cm. Arbitrarily, air is the unit referred to when the term "specific gravity" is used in speaking of a gas. If the molecular weight, $H=1$ (p. 56) of a gas be known, its specific gravity is obtained by dividing its molecular weight by 28.728. For certain purposes hydrogen is taken as the unit. As air is 14.364 times heavier than hydrogen, the sp. gr. of a gas (air=1), multiplied by 14.364 gives its sp. gr. (hydrogen=1).

In the third form of expression of specific gravities of gases, the specific gravity of oxygen is taken as 32, and the unit is a hypothetical normal gas, which is 32 times lighter than oxygen. Expressed in terms of this unit the specific gravity of a gas is called its density, and is 32 for oxygen and 2.016 for hydrogen. The density ($O=32$) may be derived from the sp. gr. (air=1) by multiplying it by 28.95. Thus the sp. gr. of oxygen: $1.1054 \times 28.95 = 32.00$.

The specific volume of a substance (V_s) is the reciprocal of its absolute density: $V_s = \frac{1}{D}$, and is the volume, in cc., which one gram occupies under normal conditions. Thus for hydrogen: $\frac{1}{.00009} = 11111$ cc., or 11.11 L., for oxygen: $\frac{1}{.001428} = 699.7$ cc., and for air: $\frac{1}{.001293} = 773.4$ cc.

Determination of Specific Gravity.—If the substance be a solid, heavier than water and insoluble therein, it is attached by a fine platinum wire to one arm of the balance, and weighed, first in air and then in water (Fig. 1). The weight in air, divided by the loss

of weight in water (which is equal to the weight of the displaced water) gives the specific gravity. If the substance be in

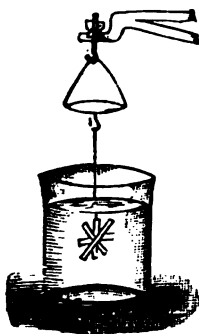


FIG. 1.

powder, the operation is similarly conducted, except that the powder is placed in a small glass or platinum bucket, whose weight in air and in water are known and subtracted from the corresponding total weights. If the solid be lighter than water, a sufficient bulk of a heavy substance, whose specific gravity is known, is attached to it, and the same method followed, the loss of weight of the heavy substance in water being subtracted from the total loss. If the substance be soluble in water its specific gravity is similarly determined with reference to some other liquid in which it is insoluble, and whose specific gravity is known. The specific gravity so obtained,

multiplied by that of the liquid used, gives the specific gravity of the solid.

To determine the specific gravity of liquids they are first brought to the required temperature, usually $15^{\circ}\text{C}.$, and the determination made with the specific gravity balance, the hydrometer, or the pycnometer.

The operation of the **specific gravity balance** depends upon the principle of Archimedes: that a body completely immersed in a liquid is subjected to an upward pressure, and consequent loss of weight, equal to the weight of the displaced liquid. The essential part of the balance is a solid glass sinker, whose volume is made exactly 1 cc., or 10 cc. The loss of weight of this sinker when immersed in a liquid, therefore, gives the specific gravity of the liquid directly with a 1 cc. sinker, and by moving the decimal point one place to the left with one of 10 cc.

The action of the **hydrometer**, which is also called by other names, such as **urinometer**, **lactometer**, **alcoholometer**, etc., according to adaptations of its graduation to special uses, is based upon the fact that a solid whose weight is less than that of an equal volume of a liquid will sink in the liquid until it has displaced a volume thereof whose weight is equal to its own. The hydrometer, is, therefore, an instrument to determine the volume of a liquid whose weight is that of the instrument. This is done by means of a graduation, which gives the specific gravities directly, upon the thin stem (Fig. 2) of the spindle,

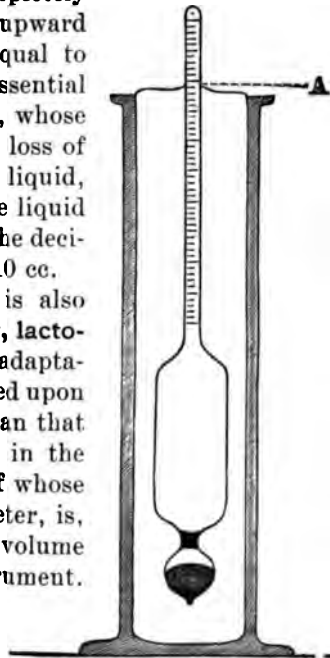


FIG. 2.

which is caused to float upright by being weighted at its lower end. Hydrometers are useful for rapid determinations in which scientific accuracy is not required, but either of the other two methods is preferable.

The **picnometer**, or specific gravity bottle, in some one of its forms, gives the most accurate results. The usual form is that shown in Fig.

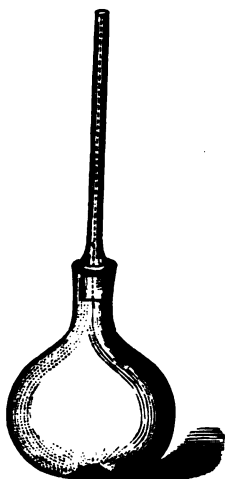


FIG. 3.

3, a bottle blown in thin glass, having a perforated stopper, which, when completely filled, contains accurately, a certain number of cc., 10, 25, 50, 100, or 1000, at 15°, and whose weight is known. When used, the bottle is completely filled with the liquid and weighed. The weight obtained, minus that of the bottle, is the specific gravity, if the bottle contain 1000 cc., $\frac{1}{10}$ if 100 cc., etc. If this form of bottle be used with a room temperature above 15° (59° Fahr.) accurate results are not obtained, owing to the expansion of the liquid and its escape and evaporation at the upper end of the stopper. To avoid this inconvenience, especially with volatile liquids, Sprengel's or Ostwald's picnometers are to be preferred, or, better, that of Riiber. The last consists of a

pipette, B, Fig. 4, with tubes *b* and *d*, of small caliber, and of exactly 20 cc. capacity. The liquid is brought to the standard temperature in the vessel A, from which the pipette is filled in the manner shown in the cut, and the excess drawn off with filter paper applied at the end of *b* until it reaches the mark on *d*. The pipette is then placed horizontally upon one pan of the balance, and the tare C, whose weight and volume both equal those of B when filled with water, is placed on the other, and the balance brought into equilibrium by weights in one or the other pan.

States of Matter.—Matter exists in the three forms of solid, liquid and gas (or vapor). The term **fluid** applies to both liquids and gases; the former being distinguished as incompressible, the latter as compressible fluids (pp. 18, 19).

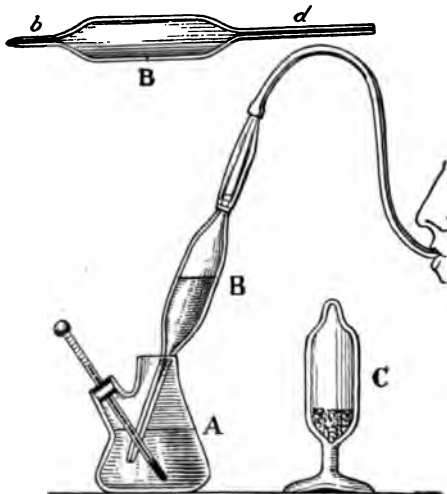


FIG. 4.

Cohesion is the force by which molecules of the same kind are held together. It is most active in solids, which therefore have definite shape and magnitude. In liquids it is much less active, yet sufficient to maintain a definite magnitude of the liquid, but it is in part overcome by gravity, which causes the liquid to assume the shape of the containing vessel. If the action of gravity be suspended, as by placing a drop of nitrobenzene in a solution of salt of the same specific gravity, cohesion causes the liquid to assume a spherical shape. In gases cohesion is almost nil; therefore, the shape and volume of any gas are those of the containing vessel. Cohesion diminishes with the addition of heat; therefore, by adding heat to a solid it is, if not decomposed, converted into a liquid and then into a gas.

SPECIAL PROPERTIES OF SOLIDS, LIQUIDS AND GASES.

Crystallization.—Solid substances exist in two forms, **amorphous** and **crystalline**. In the former they assume no geometric shape; they conduct heat equally well in all directions; they break irregularly; and, if transparent, allow light to pass through them equally well in all directions. A solid in the crystalline form has a definite geometrical shape; conducts heat more readily in some directions than in others; when broken, separates in certain directions, called **planes of cleavage**, more readily than in others; and modifies the course of luminous rays passing through it differently when they pass in certain directions than when they pass in others.

Crystals are formed in one of four ways: 1. An amorphous substance, by slow and gradual modification, may assume the crystalline form; as vitreous arsenic trioxid (*q. v.*) passes to the crystalline variety. 2. A fused solid, on cooling, crystallizes; as bismuth.

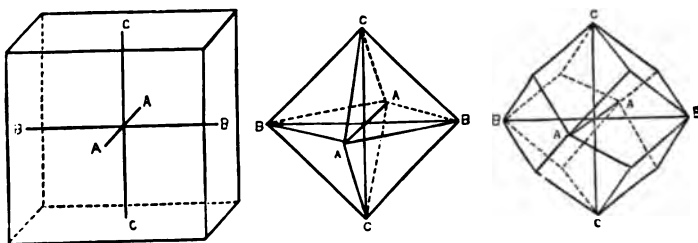


FIG. 5.

3. When a solid is sublimed it is usually condensed in the form of crystals. Such is the case with arsenic trioxid. 4. The usual method of obtaining crystals is by the evaporation of a solution of the substance. If the evaporation be slow and the solution at rest, the crystals are large and well-defined. If the crystals separate by the

sudden cooling of a hot solution, especially if it be agitated during the cooling, they are small.

Most crystals may be divided by imaginary planes into equal, symmetrical halves. Such planes are called **planes of symmetry**.

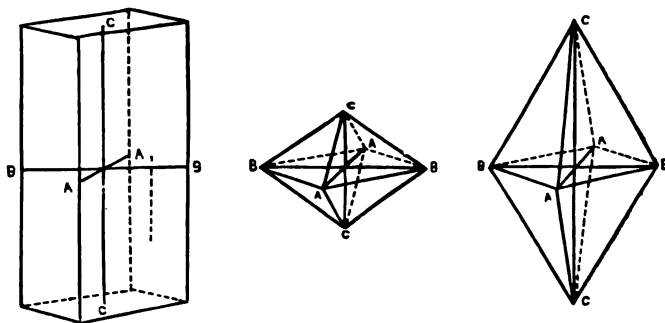


FIG. 6.

Thus in the crystals in Fig. 5 the planes $ab\ ab$, $ac\ ac$, and $bc\ bc$ are planes of symmetry.

When a plane of symmetry contains two or more equivalent linear directions passing through the center, it is called the **principal plane of symmetry**; as in Fig. 6 the plane $ab\ ab$, containing the equal linear directions aa and bb .

Any normal erected upon a plane of symmetry, and prolonged in both directions until it meets opposite parts of the exterior of the crystal, at equal distances from the plane, is called an **axis of symmetry**.

The axis normal to the principal plane is the **principal axis**. Thus in Fig. 6, aa , bb , and cc are axes of symmetry, and cc is the principal axis.

Upon the relations of these imaginary planes and axes a classification of all crystalline forms into six systems has been based.

I. The Cubic, Regular, or Monometric System.—The crystals of this system have three equal axes, aa , bb , cc , Fig. 5, crossing each other at right angles. The simple forms are the cube; and its derivatives, the **octahedron**, **tetrahedron**, and **rhombic dodecahedron**. The crystals of this system expand equally in all directions when heated, and are not doubly refracting.

II. The Right Square Prismatic, Pyramidal, Quadratic, Tetragonal, or Dimetric System contains those crystals having three axes placed at right angles to each other—two as aa and bb , Fig. 6, being equal to each other and the third, cc , either longer or shorter. The simple forms are the **right square prism** and the **right square based octahedron**. The crystals of this system expand equally only in two

directions when heated. They refract light doubly in all directions, except through one axis of single refraction.

III. **The Rhombohedral or Hexagonal System** includes crystals having four axes, three of which aa , aa , aa , Fig. 7, are of equal length and cross each other at 60° in the same plane; to which plane the fourth axis, cc , longer or shorter than the others, is at right angles. The simple forms are the regular six-sided prism, the regular dodecahedron, the rhombohedron, and the scalenohedron. These crystals expand equally in two directions when heated, and refract light singly through the principal axis, but in other directions refract it doubly.

IV. **The Rhombic, Right Prismatic, or Trimetric System.**—The axes of crystals of this system are three in number, all at right angles to each other, and all of unequal length. Fig. 6 represents crystals of this system, supposing aa , bb , and cc to be unequal to each other. The simple forms are the right rhombic octahedron, the right

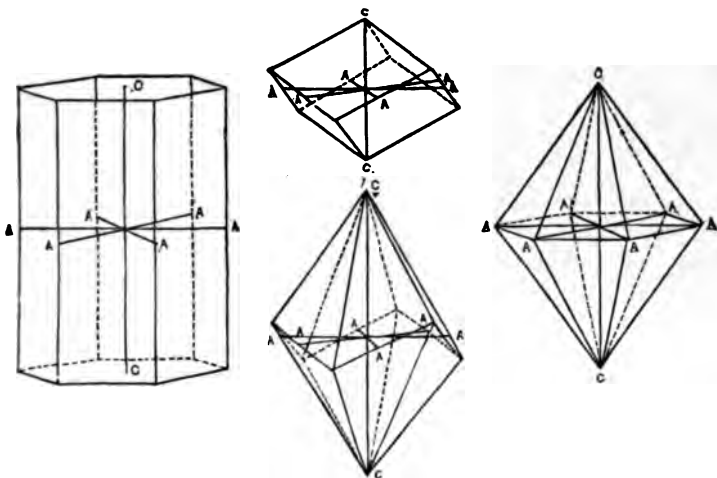


FIG. 7.

rhombic prism, the right rectangular octahedron, and the right rectangular prism. The crystals of this system, like those of the two following, have no true principal plane or axis.

V. **The Oblique, Monosymmetric, or Monoclinic System.**—The crystals of this system have three axes, two of which, aa , and cc , Fig. 8, are at right angles; the third, bb , is perpendicular to one and oblique to the other. They may be equal or all unequal in length. The simple forms are the oblique rectangular and oblique rhombic prism and octahedron.

VI. The **Doubly Oblique, Asymmetric, Triclinic, or Anorthic System** contains crystals having three axes of unequal length, crossing each other at angles not right angles; Fig. 8, *aa*, *bb*, and *cc* being unequal and the angles between them other than 90° .

The crystals of the fourth, fifth, and sixth systems, when heated, expand equally in the directions of their three axes. They refract light doubly except in two axes.

Secondary Forms.—The crystals occurring in nature or produced artificially have some one of the forms mentioned above, or some modification of those forms. These modifications, or **secondary**

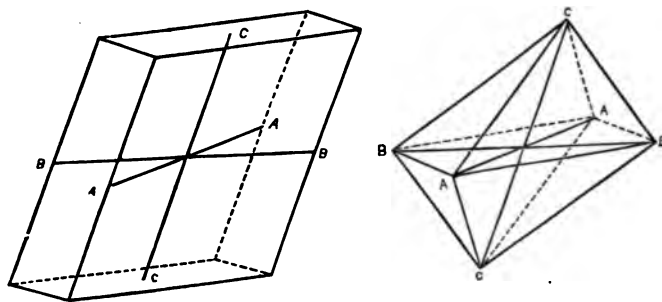


FIG. 8.

forms, may be produced by symmetrically removing the angles or edges, or both angles and edges, of the primary forms. Thus, by progressively removing the angles of the cube, the secondary forms shown in Fig. 9 are produced.

It sometimes happens in the formation of a derivative form that alternate faces are excessively developed, producing at length entire obliteration of the others, as shown in Fig. 10. Such crystals are said to be **hemihedral**. They can be developed only in a system having a principal axis.

Isomorphism.—In many instances two or more substances crystallize in forms identical with each other, and, in most cases, such substances resemble each other in their chemical constitution. They are said to be **isomorphous**. This identity of crystalline form does not depend so much upon the nature of the elements themselves, as upon the structure of the molecule. The protoxid and peroxid of iron do not crystallize in the same form, nor can they be substituted for each other in reactions without radically altering the properties of the resultant compound. On the other hand, all that class of salts known as alums are isomorphous. Not only are their crystals identical in shape, but a crystal of one alum, placed in a saturated solution of another, grows by regular deposition of the second upon

its surface. Other alums may be subsequently added to the crystal, a section of which will then exhibit the various salts, layer upon layer.

Dimorphism.—Although most substances crystallize, if at all, in one simple form, or in some of its modifications, a few bodies are capable of assuming two crystalline forms, belonging to different systems. Such are said to be **dimorphous**. Thus, sulfur, as obtained

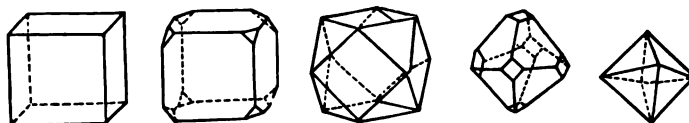


FIG. 9.

by the evaporation of its solution in carbon disulfid, forms octahedra, belonging to the fourth system. When obtained by cooling melted sulfur the crystals are oblique prisms belonging to the fifth system. Occasional instances of **trimorphism**, of the formation of crystals belonging to three different systems by the same substance, are also known.

Many substances on assuming the crystalline form, combine with a certain amount of water which exists in the crystal in a solid combination. Thus nearly half of the weight of crystallized alum is water. This water is called **water of crystallization**, and is necessary to the maintenance of the crystalline form, and frequently to the color. If blue vitriol be heated, it loses its water of crystallization, and is converted into an amorphous, white powder. Some crystals lose their water of crystallization on mere exposure to the air. They are then said to **effloresce**. Usually, however, they only lose their water of crystallization when heated (p. 115).

Allotropy.—Dimorphism apart, a few substances are known to exist in more than one solid form. These varieties of the same

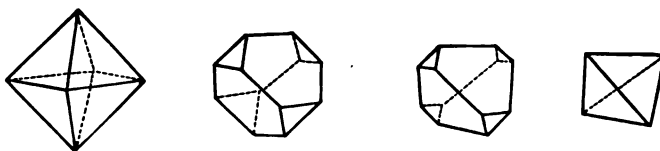


FIG. 13.

substance exhibit different physical properties, while their chemical qualities are the same in kind, but differ in their degrees of activity. Such modifications are said to be **allotropic**. One or more allotropic modifications of a substance are usually crystalline, the other or others amorphous or vitreous. Sulfur, for example, exists not only in two dimorphous varieties of crystals, but also in a third, allotropic

form, in which it is flexible and amorphous. Carbon exists in three allotropic forms: two crystalline, the diamond and graphite; the third amorphous.

In passing from one allotropic modification to another, a substance absorbs or gives out heat.

Liquids when subjected to pressure diminish in volume only to a trifling extent: mercury by 0.000003 of its volume per atmosphere. When the pressure is released, liquids regain their original volume. They are therefore perfectly elastic.

Diffusion of Liquids—Dialysis.—If a liquid be carefully floated upon the surface of a heavier liquid, with which it is capable of mixing, as brandy upon water, two distinct layers are at first formed. But, even at perfect rest, mixing of the two liquids, in opposition to gravity, will begin immediately, and progress slowly until the two liquids have diffused into each other to form a single liquid whose composition and density are the same throughout.

If, in place of bringing the two liquids into direct contact, they be separated from each other by a membrane of goldbeater's skin, each will pass through the membrane into the other, a phenomenon called **osmosis**, but they do not pass with equal rapidity. Thus, if the two liquids be alcohol and water, one part of alcohol will pass in one direction while 4.2 parts of water pass in the other. This relation, as compared with water, is the **osmotic equivalent** of the substance, and may be determined not only for liquids, but also for solids in solution.

If a layer of a pure solvent (p. 27) be similarly floated upon a solution of a solid in the same liquid, as water upon a solution of sugar, or if the two be separated by a membrane of parchment paper, bladder, or other **permeable membrane**, the pure solvent will pass into the solution, and the dissolved sugar into the pure solvent until the two liquids have the same **concentration**, i. e., contain the same quantity of dissolved substance in unit volume throughout. (See solution, p. 28.)

Solids in solution differ in the rapidity and completeness with which they undergo osmosis, or dialyse. Substances which crystallize, **crystalloids**, dialyse easily and with relative rapidity; those which do not form crystals, **colloids**, do not dialyse, or do so with extreme slowness. Advantage is taken of this difference to separate crystalloids from colloids, as salt from albumin. The solution of the two substances is placed in the inner vessel of a **dialyser** (Fig. 11), whose bottom consists of a layer of parchment paper, and the outer vessel is filled with the pure solvent, water, which is frequently changed as the crystalloid collects in it. Or a section of tubing made of parchment paper, bent into a U shape, may be used as the

inner vessel, and suspended in water. Plates of porous earthenware may also be used for dialysis of liquids which would attack an animal or vegetable membrane, but their action is much slower. **Semipermeable membranes** are membranes which are permeable to certain diffusible substances, but not to others, usually permeable to water but not to certain substances in solution in it. Such membranes exist in animal and vegetable nature and are formed artificially. Pfeffer's membrane is obtained by placing a solution of cupric sulfate in a jar of porous earthenware, which is then immersed in a solution of potassium ferrocyanid. A delicate, gelatinous film of cupric ferrocyanid forms in the walls



FIG. 11.

of the jar where the two solutions come in contact, which constitutes the semipermeable membrane, permeable to water and to saltpeter dissolved in water, but not to sugar or to many other substances in aqueous solution. (See Osmotic pressure, p. 66.)

Gases when subjected to pressure diminish in volume progressively to an amount limited only by their passage to the form of liquid (p. 29). When relieved of pressure they expand to an unlimited extent. They have, therefore, the volume of the containing vessel, upon whose walls they exert a pressure corresponding to that to which they are themselves subjected, and in all parts of which they have the same density.

Boyle-Mariotte Law.—If any gas, maintained at a constant temperature, be contained in a vessel whose capacity may be altered, as by a piston, the pressure exerted by the gas is found to be doubled when the capacity of the vessel is reduced to one-half; and corresponding variations of pressure are observed with other changes in volume:

The temperature remaining the same, the volume of a given quantity of gas is inversely as the pressure (Boyle-Mariotte Law). Or: $vp = \text{constant}$. And, denoting any two pressures under which a given weight of gas may exist by p_1 and p_2 , and the corresponding volumes by v_1 and v_2 , as p_1v_1 and p_2v_2 , both equal constant, $p_1v_1 = p_2v_2$ (p. 23). It also follows that the density of a gas (pp. 9, 10) is proportionate to the pressure.

This and other "gas laws" are only approximately true, although the departure from them, which differs with different gases, is very

slight at ordinary pressures. The greater the pressure, i. e., the more *concentrated* the gas, the wider is the departure from the rule; and the lower the pressure, i. e., the more *dilute* the gas, the smaller does it become, and the nearer does the gas approach to the state of an **ideal gas**, one which would obey the law exactly. (See p. 25.)

Mixture of Gases.—In agreement of what has been said above, if a vessel, A, containing a gas under any given pressure, be brought into communication with another vessel, B, of equal capacity, in which there is a vacuum, the gas will instantly fill both vessels equally, and in each the pressure will be one-half the original pressure.

And if the vessel B, in place of being vacuum, contain another gas, between which and the gas in A there is no chemical action, and under like pressure, the pressure in each will remain unaltered, and particles from A will rapidly pass into B, and also from B to A, until, in a very short time, this interchange of particles will produce a condition of equilibrium, and both A and B will contain the same relative proportions of the two gases.

In a mixture of gases each gas retains all of its own properties, as if the other or others were not present; and each gas is uniformly distributed throughout the space occupied.

Dalton's law of partial pressures and the third law of absorption (below) are both included in the foregoing statement. The former is to the effect that: *If the several gases composing a mixture and the mixture all have the same temperature, and if the gases severally and the mixture occupy the same volume, then the pressure exerted by the mixture will be the sum of the pressures exerted by the several gases.* And $Vp = v_1p_1 + v_2p_2 + v_3p_3 + \dots$. The pressure of each gas in the mixture is called its **partial pressure**.

Diffusion and Effusion of Gases.—If, in place of bringing two indifferent gases, of different densities and under equal pressures, into direct contact with each other, in the manner above referred to, they be separated by a porous diaphragm, mixture takes place by **diffusion** through the diaphragm, but more slowly and unequally, so that the pressures upon the two sides of the diaphragm become unequal. That gas which has the least density diffuses the most rapidly, and in such ratio that: *The quantities of gases which diffuse in unit time are inversely as the square roots of their densities.*

Effusion of a gas is its passage, not through a porous septum having a large number of minute pores, but through a single, very small opening (0.013 mm.) in a thin metallic plate. Here again the velocities of efflux of several gases are inversely as the square roots of their densities. This law is taken advantage of in an apparatus for the rapid determination of the densities of gases.

Absorption of Gases.—Physical solution (p. 27) of a gas in a liquid is called **absorption**. The absorption of gases by liquids obeys the following laws:

The weight of a gas absorbed by unit volume of a given liquid is proportionate to the gas pressure (Henry's law).

The quantity of a gas absorbed diminishes with increase of temperature.

The quantity of a gas which a liquid can absorb is independent of the nature and quantity of other gases which it may already hold in solution.

Some solid substances also absorb certain gases. Sometimes such absorption is a physical act, when it is referred to as **condensation** or **absorption**. Thus charcoal condenses about 90 times its volume of ammonia. In other cases it is a chemical combination, as when caustic potash absorbs carbon dioxide.

PHYSICAL ACTIONS OF CHEMICAL INTEREST.

HEAT.

The **Effects of Heat** upon a body are in doing *internal work*: to raise its temperature, to increase its volume, to change its state of aggregation, or to cause atomic rearrangement, i. e., chemical change, or in doing *external work*: in exerting pressure, or in transmitting heat to surrounding bodies.

Temperature.—The temperature of a body is the extent to which it can impart sensible heat to surrounding bodies. It is not to be confounded with the *amount* or *quantity of heat* which the body contains. A block of ice just beginning to melt and the same weight of water just beginning to freeze have the same temperature; but heat must be added to the ice to continue its fusion and subtracted from the water to continue its solidification, while during both processes the temperature remains the same in each.

Thermometers are instruments for the measurement of temperature. They are usually glass tubes having a bulb blown at one end and closed at the other, the bulb and part of the tube being filled with mercury or with alcohol, whose contraction or expansion indicates a fall or rise of temperature. The alcoholic thermometer is used for measuring low temperatures, and the mercurial for temperatures between -40° and 360° C. (680° F.). For higher temperatures instruments called pyrometers, based upon the expansion or variation of electrical conductance (p. 42) of solids, are used.

In every thermometer there are two *fixed points*, determined by experiment. The lower, or **freezing point**, is fixed by immersing the in-

strument in melting ice, and marking the level of the mercury in the tube upon the glass when it has become stationary. The higher, or **boiling point**, is similarly fixed by suspending the instrument in the steam from boiling water. The instrument is then graduated according to one of three scales: the **Celsius**, or **Centigrad**, the **Fahrenheit**, and the **Réaumur**. The freezing point is marked 0° in the Centigrad and Réaumur scales, and 32° in the Fahrenheit. The boiling point is marked 100° in the Centigrad, 212° in the Fahrenheit, and 80° in the Réaumur scale (Fig. 12). The space between the fixed points is divided into 100 equal **degrees** in the Centigrad scale, into 180° in the Fahrenheit, and into 80° in the Réaumur. Five degrees Centigrad are therefore equal to nine degrees Fahrenheit.

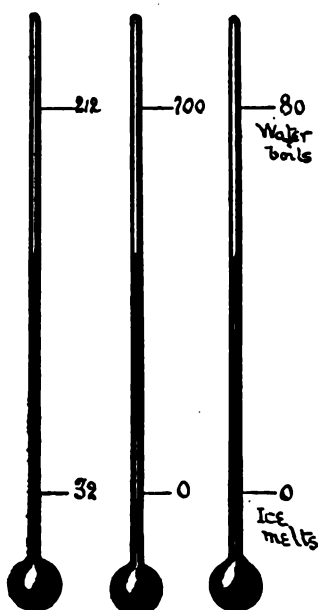


FIG. 12.

the Fahrenheit, and into 80° in the Réaumur. Five degrees Centigrad are therefore equal to nine degrees Fahrenheit.

To convert readings in one scale into terms of another the following formulæ are used:

Centigrad to Fahrenheit: Multiply by 9, divide by 5, and add 32. Example: $50^{\circ}\text{C.} \times 9 = 450 \div 5 = 90 + 32 = 122^{\circ} = \text{Ans.}$

Fahrenheit to Centigrad: Subtract 32, multiply by 5, and divide by 9. Example: $5^{\circ}\text{F.} - 32 = -27 \times 5 = -135 \div 9 = -15^{\circ} = \text{Ans.}$

The Centigrad scale is the one now exclusively used for scientific work.

Measure of Heat—Thermal Unit—Mechanical Equivalent of Heat.—Heat is measured by its effect in raising the temperature of a given weight of water through a given number of degrees of temperature. Several units have been

used, and, unless definitely stated, may easily lead to confusion.

The **calorie**, or **therm**, or **gram-calorie** (cal.) is the amount of heat required to raise the temperature of one gram of water from 0° to 1°C. (or from 4° to 5°C.). The **rational calorie** (K) is the amount of heat required to raise the temperature of one gm. of water from 0° to 100°C. , and is nearly equal to 100 cal. The **large calorie**, or **kilogram calorie** (kg:cal.), is based upon the raise of temperature of one kilogram of water from 4° to 5°C. , and is equal to 1000 cal.

The British **thermal unit** is the amount of heat required to raise the temperature of one pound (Avdp.) of water one degree Fahrenheit. And still another unit is used, based upon the pound of water and a raise of temperature of one degree Centigrad.

That mechanical motion produces heat, and that heat is a source of mechanical motion are well-known facts. It has also been experimentally demonstrated that a certain number of foot-pounds, or of ergs, of energy produce a definite number of calories of heat. The numerical relation between the amounts of heat and of mechanical motion which are interconvertible is known as **Joule's equivalent (J)**. It was first determined in terms of the British thermal unit as 772.55. That is, the amount of heat required to raise the temperature of one pound of water one degree Fahrenheit is equivalent to the work done in raising 772.55 pounds through one foot; i. e., 772.55 foot-pounds. In terms of Centigrad degrees and kilogram-meters, one gram-calorie is equivalent to 0.426 kilogram-meters. In the C. G. S. system one gram-calorie is equal to 4.18×10^7 ergs, or to 4.18 Joules (p. 8).

In place of measuring amounts of heat in calories or other similar units, they may be expressed in terms of the C. G. S. system, based upon the above equivalent, in **kilojoules (kj)**, equal to 10^{10} ergs. One kilojoule is equal to 239.1 gram-calories, and one gram-calorie to 0.004183 kilojoules.

We will use gram-calories or kilojoules in expressing amounts of heat.

Changes in Volume Caused by Heat.—As a rule, all substances increase in volume when heated, and diminish in volume on losing heat. There are, however, some exceptions to this rule.

Solids and liquids change only slightly in volume by heating or cooling. Thus the **coefficient of linear expansion**, or ratio of variation in length, of steel is .0000124, and the **coefficient of cubic expansion**, of variation in volume of mercury is .00018 for 1°C . Water on being cooled contracts until its temperature is 4°C ., between which and 0° it again expands; 4°C . is, therefore, the **temperature of maximum density of water**.

The changes in volume of gases by heat are of much greater theoretical importance than those in solids and liquids.

We have seen (p. 19) that the volume of gas varies with the pressure in obedience to the law: $VP = \text{constant}$. This is only true if the temperature remain constant. With variation in temperature the volume of a gas varies according to

The Dalton-GayLussac Law:—*The pressure remaining constant, the volume of a gas varies directly with the absolute temperature (see below). And, conversely, if the volume remain constant, the pressure varies directly with the temperature.*

The Law of Charles is to the effect that *all gases have the same coefficient of expansion.*

All gases, when cooled, contract by $\frac{1}{273}$, or 0.00367, of their

volume for each diminution of temperature of $\frac{1}{273}$ of the variation between 0° and 100° . *The coefficient of expansion (a) of all gases is, therefore, .00367 per degree Centigrad*, and is the same whatever the pressure supported by the gas. Or, the temperature remaining constant: $v = v_0 (1 + at)$, in which v is the volume at temperature t , a , the coefficient of expansion of gases, and v_0 the volume at 0°C . Or, introducing the numerical value of a : $V = v_0 (1 + .00367 t)$. In this statement it is assumed that the pressure remains constant, and the volume varies. If the volume remain constant, the pressure varies, and: $p = p_0 (1 + at)$, and $p = p_0 (1 + .00367 t)$, in which p is the pressure at temperature t , and p_0 the pressure at 0° .

Absolute Zero—Absolute Temperature.—As gases contract by $\frac{1}{273}$ of their volume with each degree of diminution of temperature, unit volume of gas at 0° on continuous cooling would occupy zero volume at -273° . As it is assumed (p. 25) that at that temperature a gas contains no heat -273° is taken as the **absolute zero**, and degrees of **absolute temperature** are from that point: $T = 273 + t$. Thus, if the observed temperature, t , be 54°C . the absolute temperature, T , is $273 + 54 = 327$. No gas is known to exist at so low a temperature as -273° ; the most resistant, hydrogen, forms a liquid which boils at -252.5° , and this temperature can only be slightly lowered by reducing the pressure. The lowest temperature yet attained is -263° .

General Gas Law.—Considering the Boyle-Mariotte and Dalton-GayLussac laws jointly, as when pressure (or volume) and temperature both vary, the two equations given above may be combined to: $p v = p_0 v_0 (1 + .00367 t)$. Or, introducing the absolute temperature: $p v = \frac{p_0 v_0}{273} T$, in which T is the absolute temperature, $t + 273^\circ$.

In comparing the volumes of gases, or in determining the relation of their weights to their volumes, these are reduced to **normal volume**, at **standard temperature**; i. e., 0°C ., and **standard pressure**; i. e., that of 76 cm. of mercury at 45° of latitude at the sea-level. These are also referred to as **normal conditions**. The reduction is made by the formula: $v_0 = \frac{v p}{76 (1 + .00367 t)}$, in which v_0 is the normal volume, v the observed volume at temperature t , and p the observed pressure in cm. of mercury.

Dynamic Theory of Heat.—It having been proven that heat and mechanical movement are convertible one into the other in certain definite quantitative relations, it may be considered as a demonstrated fact that heat is a form of energy (p. 8). And as energy may be potential or kinetic, so heat energy may be potential, as in latent heat (p. 26), or kinetic as in sensible heat. Sensible heat, tempera-

ture, is, therefore, a mode of motion. As this motion is one of invisible particles, a molecular motion, views of its nature must be theoretical. It is assumed that the motion is oscillatory, or vibratory, and that its rapidity and amplitude vary with the amount of heat; that the higher the temperature the more rapidly do the molecules vibrate, and the greater the length of their paths. This view does not preclude the possibility of rotary movements of the molecules about each other or about their axes, nor yet of movements of the atoms within the molecules (p. 53).

Kinetic Theory of Gases.—The theory stated above is in consonance with all observed facts concerning gaseous bodies; and gases offer the best material for the development of the theory, on account of the slight cohesion of their molecules and the facility with which they may be approached to or separated from each other by variation of pressure. The kinetic theory of gases assumes that the molecules of gases are spherical, perfectly elastic, extremely small in comparison to the spaces by which they are separated, and in constant vibratory movement. In this movement they occasionally collide with each other, when, by virtue of their perfect elasticity and slight cohesion, they immediately rebound so that their total path becomes a zigzag, although their "free path," i. e., the direction and distance through which they may oscillate without collision, is rectilinear, and of length dependent upon the proximity of the molecules; i. e., the pressure, or they may impinge upon the walls of the container, and rebound therefrom, and in this way produce pressure. And the pressure so produced is proportionate to the temperature (p. 23) because the rapidity of oscillation, and therefore the number of impacts in unit time increases with rise of temperature. Conversely, the rapidity and the pressure diminish with diminution of temperature, and it is assumed that at the absolute zero it ceases—there is no heat.

The velocity of motion of all the molecules in a given volume of gas is not the same. By collision with each other and with the walls of the containing vessel, the motion of some of the molecules is retarded, so that at any given temperature it is only the sum of the velocities of all the molecules present, or their average velocity, which is a constant quantity.

The departure in the action of gases from the Boyle-Mariotte law at high pressures is also in accordance with the theory. In an ideal gas, one which would obey the law accurately, the molecules would be mathematical points, without magnitude, and totally without cohesion; but, although extremely small, the molecules have magnitude, and their cohesion, although slight, is not nil, and consequently at each collision their path is not modified as it would be were the ideal conditions fulfilled: and as the molecules are closer

together, and consequently more frequently in collision, the smaller the volume of unit weight of gas, i. e., the greater the pressure, the widest departure from the law would be anticipated by the theory at high pressures, where it is found to occur (p. 19). Indeed, a formula has been constructed for the Boyle-Mariotte law (Van der Waal's formula) which takes into account the magnitude of the molecules and their cohesion, and expresses the actual conditions.

Change of State.—The state of aggregation of matter depends partly upon the pressure to which it is subjected, but principally upon the amount of heat which it contains. If chemical decomposition does not occur, when heat is added to a solid the motion of its molecules becomes more rapid, and their cohesion becomes less, until the solid becomes a liquid. With the addition of more heat the molecules are more widely separated, their cohesion is reduced to the minimum, and the liquid becomes a vapor. The reverse order of change is produced by abstraction of heat, popularly referred to as "cooling."

Solids assume the liquid form by *fusion* or by *solution*.

Fusion.—When a solid, not decomposed by heat, is sufficiently heated it *fuses*, or *melts*. Substances which withstand a high temperature without fusion are said to be **refractory**. Every substance begins to fuse at a certain temperature, which is always the same for a given substance, the pressure remaining constant, and which remains the same until fusion is complete, whatever the intensity of the heat applied. This temperature is called the **fusing point** of the substance, and is one of the characters depended upon for its identification, and as a test of its purity. Some substances pass by imperceptible changes of gradual softening from the condition of solid to that of liquid, the temperature rising the while, and therefore have no true fusing point; such are iron and glass. (See p. 29.)

The fusing point is only slightly influenced by the pressure. That of substances which contract on fusion is slightly lowered by increase of pressure, and that of those which expand on fusion is slightly raised.

Heat of Fusion—Latent Heat.—During fusion a substance absorbs heat, and during the opposite process of solidification it liberates heat, in each case without change of temperature. The amount of heat so liberated varies with different substances, and is called the latent heat of fusion of the substance. If two vessels, one containing a pound of water at $0^{\circ}\text{C}.$, and the other a pound of ice also at $0^{\circ}\text{C}.$, be both immersed in a large vessel containing hot water, the two smaller vessels will absorb equal amounts of heat, but when the ice has completely melted the temperature in that vessel will be $0^{\circ}\text{C}.$, while that in the other vessel will be $79.3^{\circ}\text{C}.$; therefore,

in the melting of the ice an amount of heat corresponding to 79.3° of temperature became latent.

Solution.—A solid, liquid or gas is said to **dissolve**, or to form a **solution** in a liquid, when the two substances form a homogeneous liquid. The molecules of the dissolved substance, the **solute**, are assumed to be uniformly distributed among the molecules of the liquid, which is called the **solvent**.

The act of solution may be a purely physical process, without chemical action between the solute and the solvent, in which case it is referred to as **physical** or **simple solution**; or it may consist of two distinct acts, one a chemical action between solute and solvent, and the other the physical solution of the new substance thus produced, in which case it is called **chemical solution**. A physical solution contains the original substance, which, if a solid, can be recovered unchanged by evaporation of the solution, as cupric nitrate from a solution of that salt, however obtained. A chemical solution is, in fact, a physical solution of the new substance formed in the reaction, as cupric nitrate is also left on evaporation of a solution of copper in nitric acid.

(For solution of gases, see Absorption, p. 21; and for solution of liquids, see Mixture of Liquids, p. 50.)

The quantity of a single solid which can be dissolved in a pure solvent, water for instance, depends upon an inherent relation between solvent and solute, called the **solubility**, and upon the temperature. The solubility of a solid is one of its distinguishing characters, and each solid has a definite solubility in a given liquid at a given temperature. When no solvent is mentioned, water is understood. The solubility is roughly qualified by the terms "freely," "readily," "sparingly," or "slightly soluble," and "insoluble." The last term is relative, as few, if any, solids are absolutely insoluble; it is applied to substances of extremely slight solubility. Numerical expression of solubility in parts by weight, is made either in parts of the solvent required to dissolve one part of the solute, or in parts of the solute contained in 100 parts of the saturated solution (below), or in parts of the solute which 100 parts of the solvent will dissolve. Some solids, such as calcium chlorid, are so readily soluble in water that they absorb sufficient from the air to form a solution. They are then said to **deliquesce**. On the other hand, calcium sulfate is usually ranked as an "insoluble" substance, its solubility being 0.254 parts in 100 at 35° .

The solubility of most solids increases with rise of temperature. With some the increase of solubility is proportionate to the rise of temperature, with others the solubility is very slightly affected by variation of temperature, and with others there is a certain tempera-

ture of maximum solubility, above which it again diminishes. Thus 35° is the temperature of maximum solubility of calcium sulfate.

A solution containing as much of the solute as it is capable of dissolving at the existing temperature is said to be **saturated**. If made at high temperature it is said to be a **hot saturated**, and if at the ordinary temperature a **cold saturated solution**. If a hot saturated solution, or one containing more solid than the liquid is capable of dissolving at a lower temperature, be cooled, the solid usually separates in the crystalline form. But if, in the case of certain substances, such as sodium sulfate, the solution be allowed to cool while undisturbed, no crystallization occurs, and the solution at the lower temperature contains a larger amount of the solid than it could dissolve at that temperature. It is then said to be **supersaturated**. If a given quantity of liquid be brought in contact with a quantity of solid less than it can dissolve at the existing temperature, the solid dissolves completely to form an **unsaturated solution**; while if it be in contact with any excess of the solid, such excess remains undissolved, and has no influence upon the solution so long as the temperature remains constant. The solubility of solids is also influenced by the pressure, but to so trifling an extent that it may be disregarded. **Dilute solutions** are such as contain very small quantities of the solutes, and the more dilute they are the more nearly do they approach the condition of **ideal solutions**; i. e., solutions which would obey certain very important laws, as an ideal gas (p. 20) would obey the Boyle-Mariotte law. (See pp. 67, 73.)

When a substance is acted upon by two immiscible solvents (p. 50), or when its solution in one such solvent is agitated with the other pure solvent, the solute, if it have the same molecular structure (pp. 52, 71) in both solutions, is distributed between the two solvents in the ratio of its solubility in each at the existing temperature, irrespective of differences in its solubility in each, and of the relative volumes of the two solvents. Thus, if varying quantities of iodine be dissolved in carbon bisulfide and the solutions agitated with water, the amounts of iodine in equal volumes of the two solutions will be in the proportion of 1 in the water to 420 in the bisulfide, irrespective of the absolute amounts of the solid and solvents present. This constant ratio between the concentrations of the two solutions is called the **coefficient of distribution**. If more than one solute be present under these conditions, each is distributed according to its own coefficient of distribution, as if the other or others were not present.

Congelation is the passage of a substance from the liquid to the solid form. It is the reverse of fusion, and takes place at the same fixed temperature, which also remains constant until fusion is com-

plete. This temperature is called the **freezing point** of the substance. During congelation an amount of heat equal to that absorbed during fusion (p. 26) is liberated.

The freezing point of a liquid holding a solid in solution is lower than that of the pure solvent. The amount of the depression is proportionate to the quantity of the solid dissolved, and varies with equal quantities of different substances. When two or more solids, having no chemical action upon each other, are in solution in the same solvent, the freezing point is lowered by an amount equal to the sum of the depressions which each would produce if present alone (p. 68).

Superfusion, or Supercooling.—Liquids, when in small volume, in the absence of the corresponding solid, and kept at rest or in very rapid agitation, may be cooled several degrees below their freezing points without solidifying. Thus water, free from air, may be cooled to -20° without forming ice. On moderate agitation, or on contact with a particle of the solid, solidification takes place instantly, the temperature suddenly rising to the freezing point (p. 99).

Vaporization.—The passage of a liquid to an aëriform state may take place from the surface of the liquid only, when the process is called **evaporation**, or it may take place throughout the mass of the liquid, when it is called **ebullition**, or **boiling**. Another difference between the two processes is that boiling, at a constant pressure, only occurs at a certain definite temperature (p. 32), while evaporation takes place, with varying activity, at all temperatures above very low ones. Thus mercury evaporates at all temperatures above -10° . Nor is evaporation limited to liquids. Solids also give off vapor, as ice does at as low a temperature as -30° . Liquids which evaporate readily, as alcohol, chloroform, ether, are distinguished as **volatile liquids**; while liquids which do not evaporate, like the fixed oils and glycerol, are called **fixed liquids**.

Gases and Vapors.—All aëriform bodies have been converted into liquids under the combined influence of cold and pressure.

Aëriform bodies exist in two conditions, dependent upon the temperature. For each gas there is a certain temperature, different for different gases, at and below which the gas can be converted into a liquid by sufficient increase of pressure, without further lowering of temperature, but above which no amount of pressure will cause liquefaction. That temperature is called the **critical temperature**. At temperatures above their critical temperatures aëriform bodies are **gases**, below that temperature they are **vapors**. When the substance is at its critical temperature there is a certain definite pressure which will cause its liquefaction, which is called its **critical pressure**. For example: the critical temperature of carbon dioxid is 31.1° , and its critical pressure 75.56 atm.

When a liquid is heated in a sealed glass tube of sufficient strength to withstand the high pressure attained, a temperature is finally reached when the liquid disappears, and the tube is filled with its vapor, which, having the same volume and weight as the liquid, also has the same density. The temperature at which this occurs, 190° for ether, is clearly the critical temperature of the substance, which is therefore also called its **absolute boiling point** (p. 24), and the pressure in the tube is its critical pressure. There is also necessarily a **critical density**, i. e., the weight of unit volume of the substance at its critical temperature and pressure.

Equilibrium between Vapors and Liquids.—The term "equilibrium" is used here, and in general in chemistry and chemical physics, to indicate a condition corresponding to the mechanical "stable equilibrium," i. e., a condition to which the system tends to return if it be disturbed.

The dynamic theory of heat (p. 24) assumes that, in their movements, the molecules may be projected beyond the free surface of a liquid, into a confined space above, and that, continuing their motion as vapor molecules, they finally may return to the liquid. The condition of equilibrium does not, therefore, imply that the passage of molecules from the liquid to the vapor (evaporation) has ceased, but that equilibrium is established when, evaporation and condensation continuing, the same number of molecules pass in unit time from the liquid to the vapor, and in the reverse direction. The condition is one of dynamic, not of static equilibrium.

If a few drops of ether be introduced into a barometric vacuum, the liquid instantly disappears, the mercury falls in the tube through a certain distance, and the space is completely filled with ether vapor. The molecules in the liquid ether, by reason of their motion (p. 25), are therefore under a certain **tension or pressure**, which causes them to assume the form of vapor when external pressure is released. In this condition, i. e., in the absence of any excess of liquid, the vapor is said to be **unsaturated**, and it then behaves like a gas, and its volume is inversely proportionate to the pressure it sustains.

If four barometer tubes, containing barometric vacua and maintained at the same temperature, be taken and a small quantity of different volatile liquids introduced into each, depressions of the mercury will be observed in all, but they will not be equal. Therefore *the vapor tensions of different liquids differ*.

If, now, further quantities of the several liquids be introduced, they continue to volatilize, and the mercury continues to fall, until a certain level is reached, differing with the several liquids, when the depression ceases, and at the same time an excess of liquid remains in the tube. The vapor now, in the presence of an excess of

the liquid, is said to be **saturated**, and behaves very differently from a gas. The difference between the height of the mercury in the tube and that of the barometer, although different with the several liquids, is constant for each liquid at a constant temperature, and is the **maximum pressure, or vapor tension of the liquid**.

If, in place of introducing different kinds of liquid into different tubes, maintained at the same temperature, the same kind of liquid be introduced into tubes maintained at different temperatures, the depression of the mercury will not be the same in them. Therefore, *the vapor pressure varies at different temperatures with the same liquid*. Thus the vapor tension of water is 4.6 mm. at 0° , and 525.5 mm. at 90° ; that of ether is 182.3 mm. at 0° , and 3898.0 mm. at 90° .

When a liquid is in contact with its saturated vapor, the vapor tension of the liquid is in equilibrium with the elastic force of the vapor, and this equilibrium is not permanently disturbed by change of volume; for, if the volume be diminished, a certain quantity of the vapor is condensed to liquid, and if the volume be increased a certain proportion of the liquid is vaporized, and, in each case, in such amount as to maintain the pressure constant at the vapor tension of the liquid for the existing temperature. Saturated vapors do not, therefore, obey the Boyle-Mariotte law. If a saturated vapor be compressed, a portion of the vapor is condensed, and if the pressure be diminished, a portion of the liquid is vaporized, in such manner that, the temperature remaining constant, the elastic force and the density of the vapor remain constant. The passage of a liquid to the form of vapor, in opposition to the elastic force of its saturated vapor, is always attended by absorption of heat, and the performance of external work, as is the case in a steam boiler.

In a mixture of a gas and a saturated vapor, the pressure of the mixture is equal to the sum of the pressures which each would exert if it occupied the space alone. Therefore, when a liquid is vaporized into an indifferent gas, such as air, evaporation continues until the partial pressure (p. 20) of the vapor is equal to the vapor tension at the existing temperature. (For vapor pressures of mixtures of liquids, see p. 50.)

When two communicating vessels are each partially filled with the same liquid at different temperatures, the vapor tension is the same in both vessels, and is that corresponding to the lower temperature. Thus, in each of two communicating vessels containing water, one at 0° and the other at 100° , the vapor pressure is 4.6 mm., although the vapor tension of water at 100° is 760 mm. The tendency to restore equilibrium causes rapid evaporation in the warmer vessel and condensation in the cooler, and is utilized in the process of **distillation**. The passage of a vapor to the form of liquid,

effected as above indicated, or by increase of pressure, is called **condensation**.

Solutions of non-volatile solids have lower vapor pressures than the pure solvent, and the amount of the depression is proportionate to certain weights of the solute (p. 68).

It is apparent that evaporation is favored by increase of temperature, by diminution of pressure, and by removal of the vapor.

Boiling.—When heat is added to a liquid its vapor pressure increases as the temperature rises, until it equals the pressure supported by the liquid, when, being in equilibrium with the external pressure, it can rise no further, and the temperature also remains stationary. Heat now added, whatever its intensity, ceases to increase the temperature, but does work in causing the liquid to **boil**. The stationary temperature of a liquid boiling at 76 cm. of atmospheric pressure is its **boiling point** (b. p.). It is always the same for a given liquid, but differs with different liquids, and is, therefore, an important character for the identification of liquids, and as a test of their purity.

As a liquid boils when its vapor pressure equals the external pressure which it sustains, the boiling point is depressed by diminution of external pressure, and raised by its increase. Thus the vapor tension of water is 92 mm. at 50°, 760 mm. at 100°, and 2 atm. (1520 mm.) at 120.6°: These temperatures are, therefore, the boiling points of water at the corresponding pressures. The distillation of liquids at reduced pressures is frequently resorted to, to avoid chemical actions which would take place at or below the boiling point, but not at the lower temperature attained by reducing the pressure; and liquids may be caused to exert certain actions above their boiling points, which they would not cause at lower temperatures, by heating them under pressure.

As boiling under standard atmospheric pressure occurs only when the vapor pressure of the liquid attains 76 cent., any cause which produces diminution of the vapor pressure delays boiling, and raises the boiling point. Such a cause, we have seen, exists in the solution of non-volatile solids in the liquid, and, therefore, such solutions have higher boiling points than the pure solvents. (See p. 68).

Sublimation.—Solids, like liquids, have vapor pressures which vary with the temperature. With most solids this pressure is extremely low at ordinary temperatures, but with others it attains the normal atmospheric pressure at temperatures not far removed from the fusing point of the solid. Solids of the latter class, such as iodine and camphor, give off vapor at ordinary temperatures, as do liquids below their boiling points, and these vapors condense in part to solids upon the walls of a closed containing vessel. The solids are

then said to **sublime**, and the condensed solid is called a **sublimate**, or, if in crystalline powder, **flowers**. The temperature at which the vapor pressure of a solid equals the normal atmospheric pressure, corresponding to the boiling point of a liquid, is called its **sublimation point**, and is usually above its fusing point. Should it be lower than the fusing point, the solid could not be fused, except under increased pressure.

Heat of Vaporization.—We have seen that a liquid, in passing to the form of vapor, absorbs a definite amount of heat, the temperature remaining constant the while. The amount of heat, expressed in calories, so required to convert one gram of the liquid into vapor, at the same temperature as the liquid, is its **heat of vaporization**, or **latent heat of vapor** (p. 26). It varies with the temperature, and, for all liquids, diminishes with increase of temperature. Thus, the heat of vaporization of water is 606.5 cal. at 0° , and 535.9 cal. at 100° . (See p. 22.)

During condensation, a vapor liberates an amount of heat equal to that which it absorbs when vaporized at its boiling point. This fact is utilized to transmit heat from one point to another by steam.

Specific Heat.—Equal weights of all substances have not the same **thermal capacity**, or capacity for heat. Or, differently expressed, it requires different amounts of heat to raise the temperature of equal weights of different substances through the same number of degrees. Thus, if equal weights of water and of mercury, both at 0° , be equally exposed to the same source of heat, when the water has acquired a temperature of 1° , the mercury will have a temperature of 30° . It, therefore, requires 30 times as much heat to raise unit weight of water through 1° as it does to raise the temperature of an equal weight of mercury equally. The unit of specific heats is the heat capacity of water, i. e., the calorie (p. 22), which is the amount of heat required to raise the temperature of one gram of water from 4° to 5° . Thus the specific heat of mercury is $\frac{1}{30} = 0.0333$.

It follows from the gas law (p. 58): $vp = RT$, that if the temperature of a given weight of gas be changed, either the volume or the pressure must also change. One factor may, however, be maintained constant, and it is not immaterial in the determination of the specific heats of gases which one is selected. For experimental reasons it is usually the **specific heat at constant pressure**, c_p , which is determined. If the determination be made at constant volume, c_v , the results are uniformly lower, owing to the rise of temperature produced by the increased pressure required to maintain the constant volume. The ratio between these two specific heats: $\frac{c_p}{c_v} = k$, is different with different gases. It is 1.4015 for air, and less than 1.667 for all gases examined.

LIGHT.

The index of refraction of substances, particularly of oils and aromatic organic liquids, is frequently utilized for their identification, and has furnished data for the determination of their molecular structure. The index of refraction is the ratio between the sine of the angle of incidence and the sine of the angle of refraction: $n = \frac{\sin i}{\sin r}$, and is determined with an instrument called a **refractometer**, or with a suitably constructed spectrometer. As the index of refraction varies with the kind of light used, and with the sp.

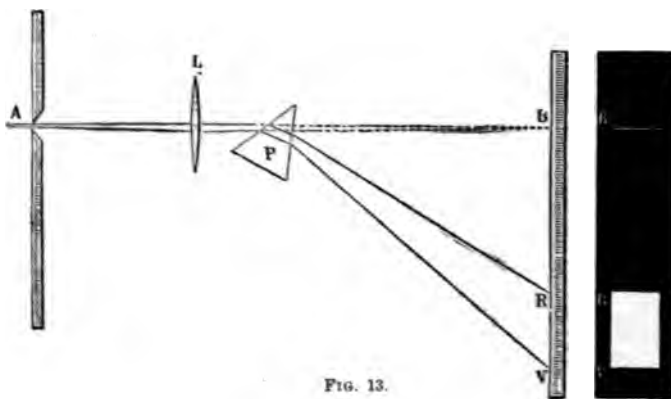


FIG. 13.

gr., therefore with the temperature, yellow (sodium) light is used, and the temperature at which the determination is made is noted in brackets. The symbol n_D is used to indicate the index of refraction for sodium light.

Spectroscopy.—A beam of white light, in passing through a prism, is not only **refracted**, or bent into a different course, but is also **dispersed**, or divided into the different colors which constitute the **spectrum** (Fig. 13). The red rays being the least deflected are the **least refrangible**, the violet rays being the most deflected are the **most refrangible**.

A spectrum is of one of three kinds: 1. **Continuous**, consisting of a continuous band of colors: red, orange, yellow, green, blue, cyan-blue, and violet. Such spectra are produced by light from white-hot solids and liquids, from gas-light, candle-light, lime-light, and electric light. 2. **Bright-line spectra**, composed of bright lines upon a dark ground, are produced by glowing vapors and gases. 3. **Absorption spectra** consist of continuous spectra, crossed by dark lines or bands, and are produced by light passing through a solid, liquid, or gas, capable of absorbing certain rays. Examples of bright-line and absorption spectra are shown in Fig. 14, p. 35.

The spectrum of sunlight belongs to the third class. It is not continuous, but is crossed by a great number of dark lines, known as **Fraunhofer's lines**, the most distinct of which are designated by letters (No. 1, Fig. 14).

The spectroscope consists of four essential parts: 1st, the slit, *a*, Fig. 15, p. 36; a linear opening between two accurately straight

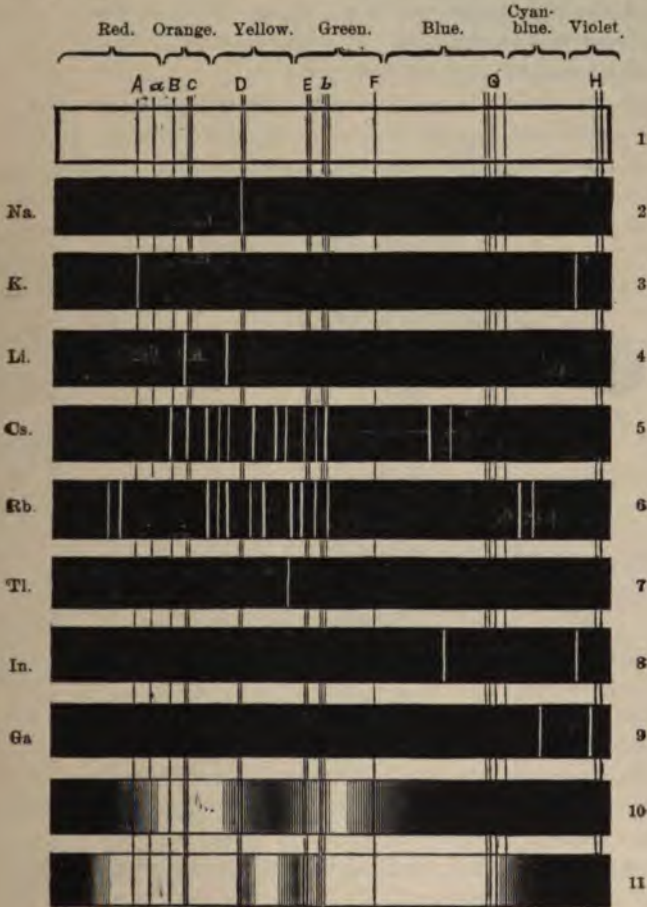


FIG. 14. 1, Solar spectrum: 10 and 11, Absorption spectra.

and parallel knife-edges. 2d, the collimating lens, *b*; a biconvex lens in whose principal focus the slit is placed, and whose object it is to render the rays from the slit parallel before they enter the prism. 3d, the prism, or prisms, *c*, of dense glass, usually of 60° , and so placed that its refracting edge is parallel to the slit. 4th, an observing telescope, *d*, so arranged as to receive the rays as they emerge from

the prisms. Besides these parts spectroscopes are usually fitted with some arbitrary graduation, which serves to fix the location of lines or bands observed.

In direct vision spectroscopes a compound prism is used, so made up of prisms of different kinds of glass that the emerging ray is nearly in the same straight line as the entering ray.

The **micro-spectroscope** (Fig. 16, p. 37) is a direct vision spectroscope used as the eye-piece of a microscope. With it the spectra of very small bodies may be observed.

As the spectra produced by different substances are characterized by the positions of the lines or bands, some means of fixing their location is required. The usual method consists in determining their

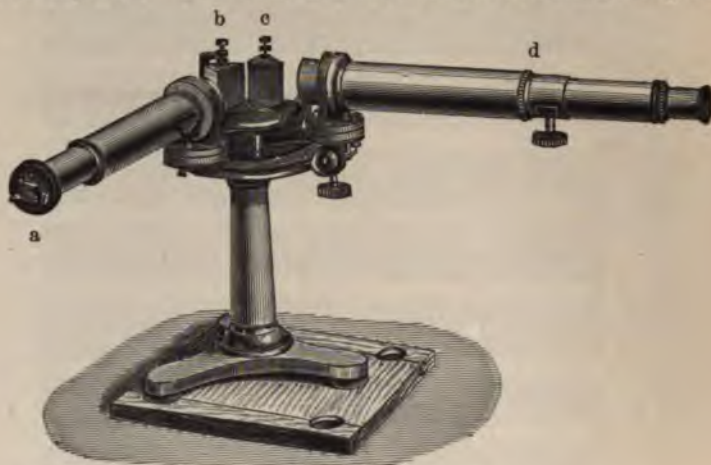


FIG. 15.

relation to the principal Fraunhofer lines. As, however, the relative positions of these lines vary with the nature of the substance of which the prism is made, although their position with regard to the colors of the spectrum is fixed, no two of the arbitrary scales used will give the same reading.

The most satisfactory method of stating the positions of lines and bands is in **wave-lengths**. The lengths of the waves of rays of different degrees of refrangibility have been carefully determined, the unit of measurement being the tenth-metre, of which 10^{10} make a metre. The wave-lengths, $=\lambda$, of the principal Fraunhofer lines, are:

A	7604.00	D	5892.12	G	4307.25
a	7185.00	E	5269.13	H ₁	3968.01
B	6867.00	b	5172.00	H ₂	3933.00
C	6562.01	F	4860.72		

The scale of wave-lengths can easily be used with any spectroscope having an arbitrary scale, with the aid of a curve constructed by interpolation. To construct such a curve, paper is used which is ruled into square inches and tenths. The ordinates are marked with a scale of wave-lengths, and the abscisses with the arbitrary scale of the instrument. The position of each principal Fraunhofer line is then carefully determined in terms of the arbitrary scale, and marked upon the paper with a $\times$ at the point where the line of its wave-length and that of its position in the arbitrary scale cross each other. Through these $\times$ a curve is then drawn as regularly as possible. In noting the position of an absorption-band, the position of its centre in the arbitrary scale is observed, and its value in wave-lengths



FIG. 16.

obtained from the curve, which, of course, can only be used with the scale and prism for which it has been made. In the Zeiss-Abbé microspectroscope (Fig. 16) a wave-length scale, Fig. 17, p. 38, photographed on glass and placed at N, is used directly. The numbers on the scale are the first two figures of those given above.

Polarimetry.—Light, in passing through many crystals in any direction other than parallel to the principal axis (p. 14), is doubly refracted, or bifurcated into two rays, the ordinary and extraordinary, of equal intensity. In then passing through a second, similar crystal, these rays are again bifurcated, forming four rays, which are of equal intensity only in two positions of the second crystal with reference to the first. If the second crystal be rotated about the common axis, two of the rays are gradually extinguished, and, on further rotation, they reappear, and the other two are extinguished. The light in passing through the first crystal has, therefore, been modified in such manner that the second crystal is opaque to the ordinary ray in one position, and to the extraordinary ray in a position opposite to the first. Light so modified is said to be polarized, and the first crystal is called the polarizer, and the second the analyzer. A Nicol's prism is a crystal of Iceland spar, so cut that it extinguishes the ordinary ray, transmitting only the extraordinary.

If, when the polarizer and analyzer are so adjusted as to extinguish a ray passing through the former, certain substances are brought between them, light again passes through the analyzer; and

in order again to produce extinction, the analyzer must be rotated upon the axis of the ray to the right or to the left. Substances capable of thus influencing polarized light are said to be **optically active**. If, to produce extinction, the analyzer is turned in the direction of the hands of a watch, the substance is said to be **dextrogyrous**; if in the opposite direction, **laevogyrous**.

The distance through which the analyzer must be turned depends upon the peculiar power of the optically active substance, the length of the column interposed, the concentration, if in solution, and the wave-length of the original ray of light. The **specific rotary power** of a substance is the rotation produced, in degrees and tenths, by

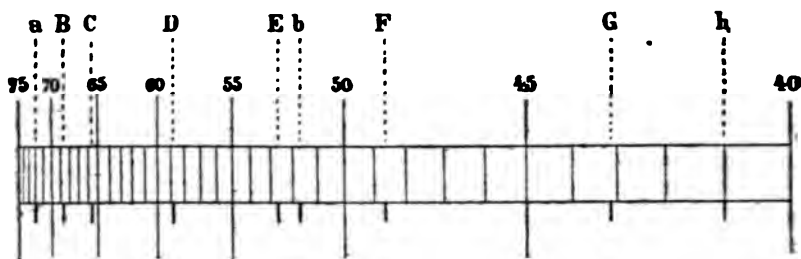


FIG. 17.

one gram of the substance, dissolved in one cubic centimetre of a non-active solvent, and examined in a column one decimetre long. The specific rotary power is determined by dissolving a known weight of the substance in a given volume of solvent, and observing the angle of rotation produced by a column of given length. Then let p = weight in grams of the substance contained in 1 cc. of solution; l the length of the column in decimetres; a the angle of rotation observed; $[a]$ the specific rotary power sought, we have

$$[a] = \frac{a}{pl}.$$

In most instruments monochromatic light, corresponding to the D line of the solar spectrum, is used, and the specific rotary power for that ray is expressed by the sign $[a]_D$. The fact that the rotation is right-handed is expressed by the sign $+$, and that it is left-handed by the sign $-$.

It will be seen from the above formula that, knowing the value of $[a]_D$ for any given substance, we can determine the weight of that substance in a solution by the formula

$$p = \frac{a}{[a]_D \times l}.$$

The polarimeter or saccharometer is simply a peculiarly constructed polariscope, used to determine the value of α .

Chemical effects of light.—Many chemical combinations and decompositions are much modified by the intensity, and the kind of light to which the reacting substances are exposed. Hydrogen and chlorine gases do not combine, at the ordinary temperature, in the absence of light; in diffused daylight or gaslight, they unite slowly and quietly; in direct sunlight, or in the electric light, they unite suddenly and explosively. The salts of silver, used in photography, are not decomposed in the dark, but are rapidly decomposed in the presence of organic matter, when exposed to sunlight.

The chemical activity of the different colored rays of which the solar spectrum is composed is not the same. Those which are the most refrangible possess the greatest chemical activity—the greatest actinic power. The visible solar spectrum represents only about one-third of the rays actually emitted from the sun. Two-thirds of the spectrum are invisible as light, and are only recognizable by their heating effects, or by chemical decompositions which they provoke.

ELECTRICITY.

Certain substances, such as amber, glass, sealing-wax, when rubbed with silk, flannel, etc., acquire the power of attracting light bodies. They are then said to be electrified.

If a glass rod be rubbed with silk and approached to a pith ball suspended by a silk thread from a glass support, the pith ball is first attracted, and, after a short contact with the glass, is then repelled. The pith ball has become electrified by contact with the glass, and in this condition the two bodies repel each other. But if now a rod of sealing-wax be rubbed with flannel and approached to the electrified pith ball, the rod will attract the ball. In this state the ball is repelled by the electrified glass, and attracted by the electrified sealing-wax. And, similarly, a pith ball electrified by contact with the electrified sealing-wax will be repelled by the wax and attracted by the glass rod. There are, therefore, two kinds of electricity, one generated in glass by friction with silk, called **vitreous** or **positive** (+) electricity, the other generated in sealing-wax by friction with flannel, called **resinous**, or **negative** (—) electricity.

Bodies similarly electrified repel each other, and bodies differently electrified attract each other.

Insulators—Conductors—Ions.—If two metal spheres, supported

upon glass rods, and placed about a foot apart, be charged, one with positive, and the other with negative electricity, the spheres will attract each other, but each will retain its charge in dry air. If, now, a glass rod be brought in contact with both spheres at the same time, each still retains its charge as before. But if a brass rod be used in place of the glass one, the positive and negative electricities neutralize each other, and both spheres lose their charges. Glass is an insulator, or non-conductor of electricity; brass is a conductor. Conductors are of two kinds: **Conductors of the first order**, such as metals, conduct electricity without themselves suffering any change, except elevation of temperature. **Conductors of the second order**, such as solutions of salts, are substances from which their constituents are separated by the passage of electricity through them. The constituents which are thus separated from a conductor of the second order are called ions (pp. 43, 72). Another distinction between the two orders of conductors is that with those of the first order electrical energy only is transported, while with those of the second order matter (the ions) is also transported.

Galvanic Electricity.—The kinetic energy (p. 8) which is developed in chemical solution of a metal (p. 27) is manifested in part as heat, but also in great part in charging the metal with negative electricity, and the solvent with positive electricity. Thus, if a plate

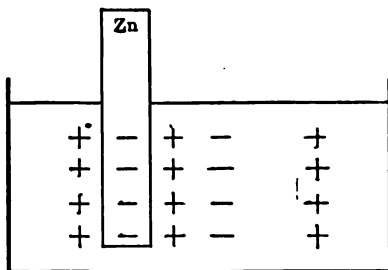


FIG. 18.

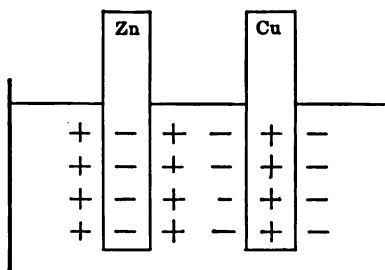


FIG. 19.

of pure zinc be immersed in pure dilute sulfuric acid, the metal becomes charged with negative electricity, and at the same time a part of the zinc goes into solution, its ions carrying a positive charge to the surrounding liquid (Fig. 18). This action continues for a very short time, until the electric charge so produced balances the "solution pressure" of the metal, i. e., its tendency to dissolve (p. 70), when all action ceases. If, now, a plate of pure copper be also immersed in the acid, the solution pressure of this metal being extremely small, the copper simply becomes charged with positive electricity, and the surrounding liquid with negative electricity; but no further solution of the zinc occurs (Fig. 19). If, now, the two

metal plates be connected by a conducting wire, the negative electricity of the zinc and the positive of the copper neutralize each other along the conductor (Fig. 20), the electric charges of the liquid recombine, and solution of the zinc again begins, attended by the generation of constantly renewed electric charges, which constantly tend to neutralize each other, producing an **electric current**, which consists of the passage of positive electricity in one direction, and of negative electricity in the opposite direction.

An arrangement of metals and solvent such as that described is called a **galvanic cell** or **element**, and a combination of two or more is a **galvanic battery**.

An electric current is produced whenever two metals, or a metal and another conducting solid, are immersed in a liquid in which the

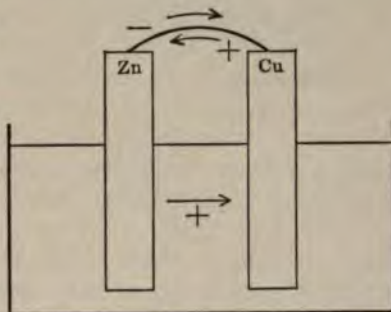


FIG. 20.

two solids have different solution pressures, or when two plates of the same kind of metal are immersed in two liquids in which the metal has different solution pressures, and either floated one upon the other, or separated only by a porous diaphragm. The metal having the higher solution pressure is the one which is dissolved in the action of the galvanic element, and hence is the position of higher potential (p. 8). The other plate is the position of lower potential. Any wires or other conductors attached to the plates are called **poles**, or **leads**, or **electrodes**. The entire system of solvent, plates and outside conductors is called an **electric** or **galvanic circuit**. The circuit is said to be **closed** when there is no break in its continuity, and the current is free to pass. It is said to be **open** when there is an interruption in its continuity, when the current ceases to pass.

The positive electrical current originates at that plate having the greater solution pressure, i. e., the higher potential (the zinc plate, Fig. 20), which is therefore called the **generating**, or **positive plate**. It flows through the liquid in the cell to the plate of lower potential (the copper plate), which is therefore called the **collecting**, or **negative plate**. From the collecting plate the current passes through the outside conductors of the circuit toward the generating plate. As the positive current leaves the cell from the negative plate, the electrode connected with that plate is of higher potential than that connected with the generating plate, and therefore we have the apparent anomaly that the pole connected with the negative plate is

called the **positive pole**, or the **anode**, while the pole connected with the positive plate is called the **negative pole**, or the **cathode**, or **kathode**. The positive current, therefore, passing from the position of higher potential to that of lower potential, in many respects resembles the flow of water from a higher to a lower level, or the passage of heat from a higher to a lower temperature. The negative current, on the other hand, passes from lower to higher potential. The total current is the sum of the passage of positive charges in one direction and of negative charges in the opposite direction.

Electromotive Force—Quantity—Resistance.—As the galvanic current is produced by the difference of solution pressures in the solvent, or activating liquid, of the substances composing the two plates, the greater this difference, which constitutes the **difference of potential** or **electromotive force**, or **voltage** (*E. M. F.*, or *E.*) of the system, is, the greater will be the **quantity** of electricity produced, and consequently, other things being equal, the greater will be the **strength** or **intensity of the current**, i. e., the quantity of electricity passing a given point in unit time.

We have seen that some substances conduct electricity, while others do not. Conductors also differ in the degree of facility with which they allow the current to pass through them when they are of equal length and of equal cross-section. The **resistance** of a conductor is the degree of opposition which it offers to the passage of the current, and the complement of the resistance is the **conductance** of the conductor. Resistance and conductance are clearly inversely proportionate to each other. They depend upon four factors: 1. The special property of conductivity of the material; 2. The length of the conductor; 3. Its cross section; 4. The temperature. The resistance is directly as the length, and inversely as the cross-section of the conductor. With metals it is increased, and with salt solutions it is diminished by elevation of temperature. In considering the resistance of a galvanic circuit we have to deal with both **internal resistance**, i. e., that of the liquid, or liquids, and plates composing the elements, and **external resistance**, i. e., that of the conducting system outside of the battery.

The **specific resistance**, or **resistivity**, of a substance is the resistance which is offered by a column of the substance one meter long and 1 sq. mm. in cross-section. Thus, if the resistivity of pure copper be taken as 100, that of silver is 94.1, that of platinum is 567, and that of mercury is 5953.3. The **specific conductance**, or **conductivity** (κ) of a substance, is the conductance of a column of the substance one centimeter long and 1 sq. cm. in cross-section.

Ohm's Law.—This fundamental empirical law is to the effect that: *The current strength is directly proportionate to the electro-*

motive force, and inversely proportionate to the resistance. — Or: $C = \frac{E}{R}$, and consequently: $R = \frac{E}{C}$, and $E = RC$, also.

Fall of Potential—Potential Gradient—Current Density.—As the positive current flows from the position of higher to that of lower potential, the potential difference is a constantly diminishing quantity; as is the "head of water" under like conditions. This diminution is referred to as the **fall of potential**, in like manner as we speak of a "fall of temperature." The amount of this fall, in units of electromotive force per centimeter of conductor, is called the **potential gradient**. It is determined by dividing the current density by the conductivity.

In an electric circuit the current is the same in every cross-section of the circuit, whether its several parts be of uniform or of varying resistivity. Consequently, if the cross-section of a portion of a uniform conductor be diminished, a larger quantity of electricity will have to pass, per unit of area of section, in the constricted part than in the wider part of the conductor. The **current density** is the current, in units of current strength, per sq. cm. of cross-section of conductor.

Divided Currents.—If a conductor be divided into two branches which are subsequently reunited at another point, and if the resistances of the two branch conductors be equal, each will carry one-half of the current; and, if the resistance of one branch, A, be double that of the other, B, A will carry $\frac{1}{3}$ of the current and B $\frac{2}{3}$: *If a conductor be divided into two or more branches subsequently reunited, the current is divided between the several branches in inverse ratio to their resistances.*

If the same, undivided, current be made to pass successively through two or more pieces of apparatus; lamps, electrolytic cells, etc., these are said to be **connected in series**, and each receives the same amount, i. e., the whole of the current. If two or more pieces of apparatus be introduced in the course of as many branches of the current, they are said to be **connected in parallel**, and each receives that proportion of the current allowed by the above rule, the resistance of the apparatus itself entering into the calculation.

Electrolysis.—We have seen (p. 40) that when a current passes through a conductor of the second order certain constituents, called ions, are separated from the conductor. This occurs with all liquids, whether solutions or fused solids, which are conductors, and the process is called **electrolysis**, while the substance acted upon, the conductor, is called an **electrolyte**. The ions are given off, one at each electrode, and entirely unmixed with each other. Those that are given off at the positive electrode, or anode, being attracted thereby,

are charged with negative electricity, and are therefore **electronegative ions**, or **anions** ('*aná*' = up, '*ω*' = to go). Those which are given off at the negative electrode, or cathode, are **electropositive ions**, or **cations** ('*κατά*' = down, or kations). Thus, when water is electrolyzed, pure hydrogen is given off at the negative electrode, and pure oxygen at the positive electrode; and when hydrochloric acid solution is electrolyzed pure hydrogen is again given off at the negative electrode, and pure chlorine gas at the positive. (See pp. 62, 70).

Polarization.—If the electrodes of a battery of sufficient electromotive force be made to terminate in two platinum plates which are immersed in water acidulated with sulfuric acid, the positive current passes from that platinum plate which is the anode to that which is the cathode, and oxygen is separated at the former and hydrogen at the latter. By adherence and penetration of these gases one platinum electrode becomes, to a greater or lesser extent, practically an oxygen plate and the other a hydrogen plate, and if now the connection with the battery be severed, and metallic connection made between the two platinum plates, a current will be found to pass in the opposite direction to that of the battery. This current is called a **polarization current**, and the electrodes are said to be **polarized**. This polarization current is, of course, produced even when the electrodes remain in the battery circuit, and, flowing in the opposite direction to the main current, tends to neutralize and weaken the latter. The accumulation of gas, or deposition of metal upon the plates of a galvanic cell also produces a polarization current in the battery itself, which is one of the causes of enfeeblement of a non-constant form of galvanic element.

Electrical Units.—*Quantity.*—In accordance with a law discovered by Faraday (p. 71), when a conductor of the second order is electrolyzed by the passage of an electrical current through it, the quantities of the ions separated in a given time are exactly proportionate to the quantity of electricity passing through the conductor. We have therefore in the mass, or weight, of some selected ion separated by a current in unit time a convenient measure of electrical quantity. The unit of this measure is called the **Coulomb (C)**, which is the quantity required to separate 0.0104 mgm. of hydrogen, or 1.1175 mgms. of silver in one second.

Current Strength.—This is the quantity of electricity passing through a conductor in unit time. The unit is called the **Ampère (A)**, which is that current strength which carries one Coulomb per second. It is also (below) that current which is produced by an electromotive force of one volt acting through a resistance of one ohm. For some purposes the ampère is inconveniently large, when the **Milliampère**, or $\frac{1}{1000}$ ampère, is used as the unit.

Voltmeters are instruments for the measurement of the quantity (Coulombs) of electricity, and, therefore, also of the current strength (Ampères). In the gas voltameter (Fig. 21) the mixture of hydrogen and oxygen (knall-gas) produced by the electrolysis of dilute sulfuric acid are collected together, and the coulombs determined from their united volume, measured in the graduated tube, reduced to normal conditions. A current of one ampère produces 10.44 cc. of knall-gas per minute. The gas voltameter has the disadvantage that the platinum electrodes soon become polarized, and the back current is a source of error. The silver voltameter gives more accurate results. It consists essentially of a rod of pure silver, serving as an anode, and immersed in a solution of silver cyanid in potassium cyanid, contained in a platinum or silver dish, or crucible, which constitutes the cathode. The coulombs or ampères are calculated from the weight of silver deposited upon the cathode in a given time. A current of one ampère deposits .0671 gm. of silver in a minute.

Galvanometers of special type, called **ammeters** (Fig. 22) are much more convenient than voltmeters, as the ampères are read off directly from an index moving over a graduated scale.

When the current is used for electrolysis, in either industrial or analytical operations, the current density at the electrodes must be carefully regulated. It is the ratio of the current strength to the surface area of the electrode (p. 41), and is expressed in terms of **normal density**, which is a current of one ampère, and an electrode area of 100 sq. cent., expressed by the symbol ND_{100} , equal to $\frac{C \times 100}{S}$, in which C is the amperage, and S the electrode area.

The current density is the same at the two electrodes only when these have equal areas. Sometimes the current density is expressed in terms of the number of ampères per square decimeter of electrode surface, expressed by the symbol D, equal to ND_{1000} .

Resistance and Conductance.—As mercury is easily obtained pure and has a high specific resistance (p. 42), the unit of resistance is derived from that of a column of definite magnitude of that

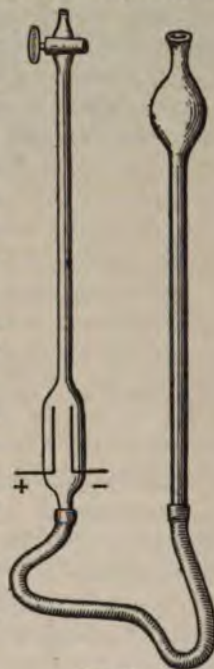


FIG. 21.



FIG. 22.

metal. The **Siemens'** unit is the specific resistance of mercury, i. e., the resistance at 0° of a column of mercury one meter long and 1 sq. mm. in cross-section. The international **Ohm** is now in more general use, and is the resistance at 0° of a column of mercury 106.3 cent. long, weighing 14.4521 gms. and having a uniform cross-section, which is 1 sq. mm. In practice, coils of insulated wire of solid metal, made of such length and cross-section as to equal the resistance of the above standard, are used. The **Megohm**, for the measurement of high resistances, is 1,000,000 ohms; and the **Microhm**, for the measurement of small resistances, is $\frac{1}{1,000,000}$ ohm.

The unit of conductance is the **Mho**, which is the conductance of a body having the resistance of one ohm.

Electromotive Force.—The unit of electromotive force is the **Volt (V)**, which is that electromotive force, which, acting steadily through a conductor having a resistance of one ohm, will produce a current of one ampère. It is also $\frac{1000}{1438}$ of the electromotive force of a normal Clark element, functioning at 15° ; or $\frac{1000}{1019}$ of that of a normal Weston element at the same temperature.

Voltmeters are galvanometers of high resistance, similar in appearance to ammeters (Fig. 22), by which the voltage is read off directly from a graduated scale.

Work—Heat—Power.—The electrical unit of work or heat is the **volt:coulomb**, which is the work done or heat generated by one coulomb over a fall of potential of one volt. One volt:coulomb is equivalent to 0.102 kg:m., and to 0.24 therm.

The unit of electrical power is the **Watt (W)**, or **volt:ampère**, i. e., the work done by a current of one ampère (one coulomb per second) under a pressure of one volt. It is equal to $\frac{1}{746}$ H. P., or 0.737 foot-pound per second, and to $\frac{1}{746}$ of a "force de cheval," or 0.102 kg:m. per second.

For the measurement of dynamo currents the watt is too small a unit, and use is made of the **kilowatt (Kw.)**, or 1000 watts as the unit. One "electric horse-power" is 1.34 kilowatts, and, with a pressure of 100 volts and a current of 10 ampères, one kilowatt is equal to 1.34 mechanical horse-power.

C. G. S. Electric Units.—One watt being equal to 0.102 kg:m. per second, and one kg:m. equal to 9.81×10^7 ergs (p. 8), one watt is equal to 10^7 ergs. From this the relation of other "practical" electrical units to C. G. S. units may be derived: 1 volt = $\frac{1}{3} \times 10^{-2}$; 1 ohm = $\frac{1}{900} \times 10^{-9}$; 1 ampère = 300×10^7 ; and 1 coulomb = 300×10^7 electrostatic, or C. G. S. units. The equivalents in electromagnetic units are: 1 volt = 10^8 ; 1 ohm = 10^9 ; 1 ampère = 10^{-1} ; and 1 coulomb = 10^{-1} .

CHEMICAL PHENOMENA.

Elements.—The great majority of material substances existing in nature, or produced artificially, may be so decomposed as to yield two or more other substances, different in their properties from the substance from which they originated, and from each other; and in such decomposition the weight of each of the products separately is less than that of the original substance, which latter is, however, equal to the sum of the weights of the new substances. Thus, if we heat 216 grams of a solid, red powder, mercuric oxid, it disappears completely, and in its place there may be collected 16 grams of a colorless gas, and 200 grams of liquid, metallic mercury. Or, if 18.016 grams of water be decomposed by electrolysis, there may be collected 16 grams of the same kind of gas, oxygen, as was obtained from the mercuric oxid, and 2.016 grams of a much lighter, inflammable gas, hydrogen. Although mercury, oxygen and hydrogen may be obtained from many sources, they have never been split up to yield two other dissimilar substances. They are **simple**, or **elementary substances**, or **elements**: i. e., *substances which cannot by any known means be split up into other, dissimilar, substances.*

Although hundreds of thousands of different species of material substance are known to exist, but eighty of these are elements (list p. 55; see also p. 103).

Non-elementary Substances,—Mechanical Mixtures.—All material substances which are not wholly elementary are made up of elements, or compounds (below), or both, aggregated together in one of three different conditions: as **mechanical mixtures**, as **chemical compounds**, or as **physical mixtures** (p. 54).

Speaking strictly, only elementary substances are homogeneous, i. e., alike in all their parts, down to the most minute particles, their atoms. Speaking relatively, mechanical mixtures are heterogeneous, while compounds and physical mixtures are homogeneous.

In **mixtures**, whether mechanical or physical, the constituent substances retain their individual properties unaltered in kind, and they may be mingled in any quantitative proportions, except that in simple solutions, which are physical mixtures, such proportions are confined within definite limits. Therein they differ from compounds.

The particles of which a **mechanical mixture** is composed, if sufficiently different in appearance, may be distinguished from each other by vision, sometimes with the unaided eye, as the particles of feldspar, mica and quartz, of which granite is composed, or microscopically, as the particles of an intimate mixture of two finely divided powders of different colors. The ingredients of a mechanical mixture may also be separated from each other without the expendi-

ture of much work, by physical or mechanical means. Thus, the particles of iron may be removed with a magnet from the most intimate mixture of finely powdered iron and sulfur; or, the ingredients of a medicinal "mixture" may be separated by the centrifuge. With mechanical mixtures chemistry has no concern until after their separation into their constituents, and only with these as elements or compounds.

Compounds.—Many substances, when examined as to their composition, are found to consist of two or more elements, always combined in the same proportion, the constituent elements differing essentially in their properties from the original substance. Such substances are chemical compounds. Thus, when water is decomposed, as by electrolysis, it always yields 88.81 per cent, by weight, of the gaseous supporter of combustion: oxygen, and 11.19 per cent of the inflammable gas: hydrogen. And when common salt is decomposed it is found to consist of 39.4 per cent of a white, soft, metal: sodium, and 60.6 per cent of a yellowish, suffocating gas: chlorine. And similarly, a vast number of compounds have been examined, and each has always been found to consist of the same elements in the same proportions.

These facts are summarized in the **Law of Definite Proportions**: *The relative weights of elementary substances in a compound are definite and invariable.*

But something more than a definite proportion of the constituent elements is necessary to constitute a compound. When water is electrolyzed, and the products are collected separately, one volume of oxygen is obtained for every two volumes of hydrogen (or in the proportions by weight given above). But if the products be collected in the same vessel a mixture of the two gases, known by the German name of "knall-gas," is obtained, which has always the same definite composition as the water from which it was derived. But if equal weights of "knall-gas" and of water vapor be examined they will be found to differ widely in their properties. If examined at 110° both will have the same appearance, as transparent, colorless gases, and each can be demonstrated to be homogeneous. But if they be cooled to 90° , the water vapor will condense entirely to liquid water, while the knall-gas will remain gaseous. Or, if each be brought into a diffusion apparatus for a short time, at a temperature maintained above 100° , the water vapor which passes through will be identical in every respect to that which does not, while, with the knall-gas, that portion of the gas which diffuses will exhibit the properties of hydrogen, while that which does not will have the properties of oxygen. Or, if an electric spark be passed through the water vapor and through the knall-gas, it produces a violent explosion in the

latter, but no effect in the former. The knall-gas is a physical mixture of hydrogen and oxygen, the vapor of water, a chemical compound of the same in the same proportions. *The compound has properties of its own, distinct from those of the constituent elements.*

While a given compound always contains the same elements in the same proportions, elements may combine with each other in more than one proportion. Thus oxygen and nitrogen combine with each other in five different ratios. In the five compounds thus formed the two elements bear to each other the following relations by weight:

- In the first, 14 parts of nitrogen to 8 of oxygen.
- In the second, 14 parts of nitrogen to $8 \times 2 = 16$ of oxygen.
- In the third, 14 parts of nitrogen to $8 \times 3 = 24$ of oxygen.
- In the fourth, 14 parts of nitrogen to $8 \times 4 = 32$ of oxygen.
- In the fifth, 14 parts of nitrogen to $8 \times 5 = 40$ of oxygen.

and similar simple ratios are found to exist in the compounds formed whenever two elements combine with each other in more than one ratio. These facts are generalized in the **Law of Multiple Proportions**: *When two elements combine with each other to form more than one compound, the resulting compounds contain simple multiple proportions of one element as compared with a constant quantity of the other.*

If the proportions in which elements combine together, in accordance with the above laws, be compared with each other, it is found that the mathematical axiom that "things which are equal to the same thing are equal to each other" holds good. For example: 70.9 parts of chlorine combine with 40.1 parts of calcium, and 16 parts of oxygen also combine with 40.1 parts of calcium; therefore, 70.9 parts of chlorine combine with 16 parts of oxygen, or the two elements combine in the proportion of some simple multiples of 70.9 and 16. This relation is expressed in the **Law of Reciprocal Proportions**: *The ponderable quantities in which substances unite with the same substance express the relation, or a simple multiple thereof, in which they unite with each other.* This law applies to reactions between compounds as well as to combinations of elements.

Physical Mixtures.—Mixtures of gases, of vapors, of gases and vapors (p. 29), of liquids, and sometimes of solids, and solutions, are **physical mixtures**. They differ from mechanical mixtures in that they are homogeneous, in the sense that the proportions of the constituents are the same in all parts of the mixture; and in that the separation of the constituents of a physical mixture requires the expenditure of a notably greater amount of work than is required to produce the like result with a mechanical mixture.

Mixtures of gases (p. 20) and of **unsaturated vapors** (p. 30) may be made in any proportions, and in them each constituent retains its

own properties as if the other were not present. The mixing is not attended by elevation of temperature, unless there be chemical action between the constituents, when the temperature usually rises, although in some cases it falls (p. 97).

Some few pairs of liquids mix together in all proportions, as do alcohol and water, or ether and carbon bisulfid. But more usually there is a limit to the proportion of one liquid which another will dissolve. If small proportions of ether be gradually added to water and the mixture be agitated, the ether at first dissolves in the water, forming a homogeneous liquid, and this continues until the water becomes saturated with ether, when two layers appear, the lower water saturated with ether, the upper ether saturated with water. On further addition of ether, the water layer diminishes to disappearance, during which time the condition of saturation of each liquid with the other persists. On continuing the addition of ether, a more and more dilute solution of water in ether is obtained.

The adjective "immiscible" as applied to two liquids is not absolute, but is used in speaking of two liquids, like ether and water, which separate into two layers after agitation, provided one be not present in great excess, each being, when so separated, a saturated solution of the other.

Of the physical properties of mixtures of liquids only one, the mass, is strictly "additive": the weight of a mixture is the sum of the weights of its components. The quantitative value of all other physical characters of a mixture of liquids, volume, specific gravity, specific heat, color, refractive index, etc., vary slightly, but only slightly, from the algebraic sum of those of the constituents. Thus, when alcohol and water are mixed, a condensation occurs, which varies in amount with the proportions, and is at the maximum with 52.3 volumes of alcohol to 47.7 volumes of water, which make, not 100 volumes, but 96.35 volumes. Frequently a physical character possessed by a liquid, e. g., specific rotary power, is modified to a varying extent, otherwise than by mere dilution, by admixture of another liquid not possessed of this property. Possibly these departures depend upon the occurrence of some degree of chemical combination, as would appear to take place in the case of the alcohol and water above, in which the proportions named are about those which would be required by the composition of one molecule of alcohol to three molecules of water (p. 52); and in which the mixing is attended by slight elevation of temperature (p. 98).

The vapor pressure of a mixture of two liquids, A and B, depends, not only upon the vapor pressures of two liquids, but also upon the solubility of the vapor of A in the liquid B, and that of the vapor of B in A. When the two liquids are practically insoluble in

each other, as water and carbon bisulfid, the vapor pressure of the mixture is very nearly the sum of the vapor pressures of the constituents at the same temperature. When the two liquids are soluble in each other to a certain degree, as ether and water, the vapor pressure of the mixture is much smaller than the sum of those of the two liquids. In the case of ether and water it is less than that of the ether alone. When two liquids mix in all proportions, as water and alcohol, the vapor pressure of the mixture is intermediate between those of the constituents; and in such a mixture the vapor pressure, and consequently the boiling point, varies with the proportions of the two constituents. On heating such a mixture at constant pressure, and condensing the vapor (distilling it), the first products condensed will contain a larger proportion of the more volatile constituent, and the less volatile will accumulate in the liquid mixture, whose vapor pressure will therefore fall, and whose boiling point will consequently rise. This is taken advantage of to separate two liquids of different boiling points by "fractional distillation." But *complete* separation by this means is possible only when the vapor of one liquid is readily soluble in the other liquid, but the vapor of the second is difficultly soluble in the first. Only in this case is the fall of vapor pressure *continuous*; under other conditions, the variation of vapor pressure is not represented by a straight line, but by a curve, in consequence of which either the distillate or the residual liquid remains a mixture. In no case can separation by fractional distillation be effected with any degree of completeness by a single operation; repeated "fractionings" are required.

Mixtures of solids are usually mechanical mixtures (p. 47), but in some instances the particles of solid mixtures are so intimately intermingled that the products are referred to as **solid solutions**. Indeed, when one constituent predominates largely, there is reason to believe that "dissociation" may occur, as in dilute liquid solutions (p. 70). **Isomorphous mixtures** are crystals obtained by evaporation of mixed solutions of isomorphous compounds (p. 16), such as the alums, which crystals contain the several salts, homogeneously distributed throughout, and in any proportions. Metallic alloys, glasses, and probably dyed fibers are solid solutions.

For liquid solutions, see pp. 27, 28.

Combination of gaseous elements by volume.—The laws of definite proportions, of multiple proportions, and of reciprocal proportions, also known as the laws of Richter, Dalton and Wenzel, respectively (pp. 48, 49), refer to proportions *by weight* in which elements unite to form compounds.

When the proportions *by volume* in which gaseous elements combine to form compounds are compared with each other and with the

volumes of the gases produced, all at the same temperature and pressure, simple relations are also found to exist, which are expressed in the laws of GayLussac:

First.—*There exists a simple relation between the volumes of gases which combine with each other.*

Second.—*There exists a simple relation between the sum of the volumes of the constituent gases, and the volume of the gas formed by their union.* For example:

- 1 volume chlorin unites with 1 volume hydrogen to form 2 volumes hydrochloric acid.
- 1 volume oxygen unites with 2 volumes hydrogen to form 2 volumes vapor of water.
- 1 volume nitrogen unites with 3 volumes hydrogen to form 2 volumes ammonia.
- 1 volume oxygen unites with 1 volume nitrogen to form 2 volumes nitric oxid.
- 1 volume oxygen unites with 2 volumes nitrogen to form 2 volumes nitrous oxid.

It will be noted that hydrogen combines with chlorin, oxygen and nitrogen in the respective proportions by volume of 1:1, 2:1 and 3:1. Also, that, while the volume of the compound of hydrogen and chlorin is equal to the sum of the volumes of the components, in the formation of the compound with oxygen there is a condensation in volume of one-third, and of that with nitrogen of one-half.

Molecular and Atomic Theories.—**Postulate of Avogadro, or of Ampère.**—In explanation of the facts just cited (as well as of many others), it is assumed that matter is not infinitely divisible, that there is a certain *smallest quantity of any substance which can exist in the free state*, which is called the **molecule**. With regard to compound substances (p. 48), this is more than a mere assumption, for, considering the smallest quantity of a compound, however small it may be, it still retains the properties of the compound, but it contains at least two smaller magnitudes, of substances whose properties differ from those of the compound, i. e., those of the elements of which it is composed, and, therefore, it cannot itself be infinitely small. The molecule of hydrochloric acid contains both hydrogen and chlorin, and, however small it may be, the whole must be greater than either of its parts, and it must therefore have a definite magnitude.

Almost simultaneously, in 1811 and 1812, Avogadro and Ampère based upon the facts described in the laws of GayLussac the postulate that *equal volumes of all gases, under like conditions of temperature and pressure, contain equal numbers of molecules*.

This is usually referred to as the "law" of Avogadro, or of Ampère. It has, however, not the force of a scientific "law," which, like the laws above quoted, is simply a generalized statement of a series of observed and proven facts. This statement, being based upon the undemonstrable assumption of the existence of molecules, is

no more capable of proof than is the postulate of Euclid, that "a straight line may be drawn between any two points." But this postulate of Avogadro has proven itself to be of enormous utility in the development of both chemistry and physics; and its close and uniform accordance with the results of both physical and chemical investigations, and with the modern kinetic theory of gases lends it additional support.

Applying the postulate of Avogadro to the laws of GayLussac, we may translate the first three combinations given in the table on page 52, into the following:

- 1 molecule chlorine unites with 1 molecule hydrogen, to form 2 molecules hydrochloric acid.
- 1 molecule oxygen unites with 2 molecules hydrogen, to form 2 molecules vapor of water.
- 1 molecule nitrogen unites with 3 molecules hydrogen, to form 2 molecules ammonia.

But the ponderable quantities in which these combinations take place are:

- 35.5 chlorine to 1 hydrogen.
- 16 oxygen to 2 hydrogen.
- 14 nitrogen to 3 hydrogen.

And as single molecules of hydrogen, oxygen and nitrogen are in these combinations subdivided to form 2 molecules of hydrochloric acid, water and ammonia, it follows that these molecules must each contain two equal quantities of hydrogen, oxygen and nitrogen, less in size than the molecules themselves. And, further, as in these instances each molecule contains two of the smaller quantities, or atoms, the relation between the weights of the molecules must also be the relation between the weights of the atoms, and we may therefore express the combinations thus:

- 1 atom chlorine weighing 35.5 unites with 1 atom hydrogen weighing 1;
- 1 atom oxygen weighing 16 unites with 2 atoms hydrogen weighing 2;
- 1 atom nitrogen weighing 14 unites with 3 atoms hydrogen weighing 3;

and consequently, if the atom of hydrogen weighs 1, that of chlorine weighs 35.5, that of oxygen 16, and that of nitrogen 14.

Assuming, then, the existence of molecules and atoms, the distinction between them may be expressed in the following definitions:

A molecule (M) is the smallest quantity of any substance that can exist in the free state.

The molecules of all substances are made up of atoms, upon whose nature, number and arrangement with regard to each other the properties of the substance depend. In elementary substances the atoms

are all of the same kind. The molecules of compound substances contain at least two atoms different in kind.

An atom is the smallest quantity of an elementary substance which can enter into the composition of a molecule.

The word "atom" can only be used in speaking of an elementary substance, and then only as a constituent of a molecule or while passing through a chemical reaction. When liberated, atoms usually unite to form other molecules, although there are a few elements whose molecules consist of single atoms.

In the light of the molecular and atomic theories the distinction between mechanical mixtures, physical mixtures and compounds may be made more briefly than by the statements on pp. 47, 48, by saying that the first are mixtures of masses, the second mixtures of molecules, and the third compounds of atoms.

Atomic Weight.—The atoms of the several elements have definite relative weights, and upon the accurate determination of these all methods of quantitative chemical analysis depend. (See Stoichiometry, p. 78.) Clearly, as the atomic weights are *relative*, the weight of one atom of any element may be selected as the unit or base in terms of which the weights of the atoms of other elements may be expressed. Formerly the unit adopted was the weight of one atom of the lightest known substance, hydrogen, and the atomic weight of an element represented the weight of one atom of that element as compared with the weight of one atom of hydrogen.

But the determination of the atomic weight of an element depends upon accurate analyses of compounds of that element, and hydrogen, unfortunately, forms compounds amenable to accurate analysis with but few other elements. Oxygen, on the other hand, forms compounds with a great number of other elements, and determinations of atomic weights have usually been made with reference to oxygen in the first instance. If expressed in terms of $H=1$, therefore, their accuracy depends upon the correctness of the determination of the ratio between the atomic weights of oxygen and of hydrogen, which, according to the most recent determination, is $H:O::1:15.88$ or $O:H::16:1.008$. But this ratio cannot be considered as being definitely decided; therefore, to avoid the necessity of a recalculation of all atomic weights with increased accuracy of the determination of the ratio $O:H$, chemists have agreed that the atomic weight of oxygen be taken as the base of the system at 16. In this system the atomic weight of hydrogen becomes 1.008, or for ordinary purposes 1.01. An incidental advantage of this system is that the atomic weights are more frequently integral numbers than with the system in which $H=1$, as will be seen in the following table, in which both systems are given:

ELEMENTS

NAME	Symbol	O=16	H=1	NAME	Symbol	O=16	H=1
Actinium . . .	Ac	. . .	. . .	Molybdenum . .	Mo	96.	95.3
Aluminium . . .	Al	27.1	26.9	Neodymium . .	Nd	143.6	142.5
Antimony . . .	Sb	120.2	119.3	Neon	Ne	20.	19.9
Argon	A	39.9	39.6	Nickel	Ni	58.7	58.3
Arsenic	As	75.	74.4	Nitrogen	N	14.04	13.93
Barium	Ba	137.4	136.4	Osmium	Os	191.	189.6
Bismuth	Bi	208.5	206.9	Oxygen	O	16.000	15.88
Boron	B	11.	10.9	Palladium	Pd	106.5	105.7
Bromin	Br	79.96	79.36	Phosphorus . . .	P	31.	30.77
Cadmium	Cd	112.4	111.6	Platinum	Pt	194.8	193.3
Cæsium	Cs	132.9	131.9	Potassium	K	39.15	38.85
Calcium	Ca	40.1	39.7	Praseodymium . .	Pr	140.5	139.4
Carbon	C	12.	11.91	Radium	Ra	225.	223.3
Cerium	Ce	140.25	139.2	Rhodium	Rh	103.	102.2
Chlorin	Cl	35.45	35.18	Rubidium	Rb	85.5	84.9
Chromium	Cr	52.1	51.7	Ruthenium	Ru	101.7	100.9
Cobalt	Co	59.	58.55	Samarium	Sm	150.3	149.2
Columbium	Cb	94.	93.3	Scandium	Sc	44.1	43.8
Copper	Cu	63.6	63.1	Selenium	Se	79.2	78.6
Erbium	Er	166.	164.8	Silicon	Si	28.4	28.2
Europium	Eu	151.79	150.58	Silver	Ag	107.93	107.11
Fluorin	F	19.	18.9	Sodium	Na	23.05	22.88
Gadolinium	Gd	156.	154.8	Strontium	Sr	87.6	86.94
Gallium	Ga	70.	69.5	Sulfur	S	32.06	31.82
Germanium	Ge	72.5	72.	Tantalum	Ta	183.	181.6
Glucinium	Gl	9.1	9.03	Tellurium	Te	127.6	126.6
Gold	Au	197.2	195.7	Terbium	Tb	160.	158.8
Helium	He	4.	4.	Thallium	Tl	204.1	202.6
Hydrogen	H	1.008	1.000	Thorium	Th	232.5	230.8
Indium	In	115.	114.1	Thulium	Tm	171.	169.7
Iodin	I	126.97	126.01	Tin	Sn	119.	118.1
Iridium	Ir	193.	191.5	Titanium	Ti	48.1	47.7
Iron	Fe	55.9	55.5	Tungsten	W	184.	182.6
Krypton	Kr	81.8	81.2	Uranium	U	238.5	236.7
Lanthanum	La	138.9	137.9	Vanadium	V	51.2	50.8
Lead	Pb	206.9	205.35	Xenon	Xe	128.	127.
Lithium	Li	7.03	6.98	Ytterbium	Yb	173.	171.7
Magnesium	Mg	24.36	24.18	Yttrium	Yt	89.	88.3
Manganese	Mn	55.	54.6	Zinc	Zn	65.4	64.9
Mercury	Hg	200.	198.5	Zirconium	Zr	90.6	89.9

In some cases the results of analyses are such as would agree with two values as the atomic weight equally well. In this case we can decide which is the correct value by the law of Dulong and Petit: The product of the specific heat (p. 33) of any solid element into its atomic weight is approximately a constant number. This number, known as the **atomic heat**, varies between 5.39 and 6.87. When the chemical relations indicate either one of two numbers as the atomic weight, that one is selected which, when multiplied by the specific heat, gives an atomic heat within the above limits.

The atomic heats of those elements which exist in two or more allotropic modifications (p. 17) vary in the several forms, and at

different temperatures, and fall outside of the above limits. Thus the atomic heat of crystallized boron is 2.11 at -39.6° , and 3.99 at 233.2° , while that of amorphous boron is 2.81; that of the diamond is 0.76 at -50.5° , and 5.51 at 985° , while that of graphite is 1.37 at -50.3° , and 5.60 at 978° .

Molecular Weight.—We have seen (p. 53) that in the formation of hydrochloric acid, water and ammonia, the molecules of hydrogen each contribute one-half of their material to the formation of each of the several new molecules. The molecules of hydrogen must, therefore, contain at least two atoms each; and it can also be shown that the molecules of chlorine, oxygen, nitrogen and, in fact, of most other elements also contain at least two atoms each. There are exceptions, however, in the cases of several metals, whose molecules consist of single atoms.

Taking the weight of one atom of hydrogen as the basis of molecular as well as of atomic weights *the molecular weight (MW) of a substance is the weight of its molecule as compared with the weight of an atom of hydrogen*. It is immaterial to this definition what the absolute weight of the hydrogen atom may be, or whether it is considered as weighing 1.000 or 1.008. The molecular weight is also, obviously, the sum of the weights of the atoms making up the molecule.

A ready method for determining the molecular weights of substances existing or obtainable in the aëriiform state is based upon the postulate of Avogadro. The specific gravity of a gas or vapor referred to hydrogen is the weight of any given volume as compared with the weight of an equal volume of hydrogen (p. 10). But equal volumes contain equal numbers of molecules (p. 52), and the relation of weights, the sp. gr., of the whole is the same for any equal fractions, down to the molecules, and therefore this specific gravity is the weight of a molecule of the gas as compared with that of a molecule of hydrogen; and as the molecule of hydrogen contains two atoms, while one atom is the unit of comparison, it follows that *the specific gravity of a gas compared with hydrogen, multiplied by two, is its molecular weight*.

The same principle is more directly applied by the use of the **density** of gas (p. 10) in place of its sp. gr. ($H=1$). *The density of a gas or vapor ($O_2=32$) is its molecular weight ($H=1.008$)*. By this method, also, the molecular weight is directly referred to the system of atomic weights in which $O=32$, $H=1.008$, etc. (p. 55), and the molecular weights of hydrogen, oxygen, hydrochloric acid, and water are found to be 2.016, 32, 36.458 and 18.016, respectively.

If the absolute density (p. 9) of a gas be known, its molecular weight, or density, is obtained by dividing this by the absolute density of the normal gas (p. 10). As the normal gas is assumed to be 32

times lighter than oxygen, and 1 L. of oxygen at 0° and 76 cent. weighs 1.4291 gms. the absolute density of the normal gas for 1cc. is $\frac{.0014291}{32}$ or .00004466 gm. Therefore the weight of a liter of gas at 0° and 76 cent., divided by .04466, is its molecular weight. Thus for chlorin $\frac{3.167}{.04466} = 70.9$. Or the determination may be made with any volume of gas, V in cc., at any temperature, t in C° , and any pressure, p in cent. Hg, by ascertaining its weight, P in gms., by the formula: $M = 6232 \frac{(273+t) P}{p v}$. Thus 500cc. oxygen at 15° and 76 cent. weigh 0.6773 gm.; therefore $M = 6232 \frac{288 \times .6773}{76 \times 500} = 31.99$.

When a substance cannot be volatilized unchanged, its molecular weight may be determined from certain properties of its solutions, which will be considered under the head of "Osmotic Pressure" (p. 66).

Gram-molecule — Mol.—That quantity of a substance whose weight is represented by its molecular weight expressed in grams is called a **gram-molecule**, or **mol**; as 32 gms. oxygen, 70.9 gms. chlorin, 18.016 gms. water.

The mol is a quantity both theoretically and practically important. We have now to consider it in connection with certain facts already referred to.

Molecular Volume.—The molecular volume of a gas or liquid is the volume occupied by one mol of the substance under normal conditions.

According to the postulate of Avogadro (p. 52), equal molecular weights (mols) of all gases must occupy the same volume, at the same temperature and pressure, or, in other words: *the molecular volume (V_m) of gases is a constant quantity*. The molecular volume of a gas is the product of its specific volume (V_s), i. e., the volume in cc. which 1 gm. occupies at 0° and 76 cm. (p. 10), and its molecular weight. Thus

	Weight of 1 L in gms. at 0° and 76 cm.	V_s	Mw.	$V_s \times Mw$, in L.
Hydrogen	0.08988	11,111	2.016	22.399
Oxygen	1.4291	699.7	32.000	22.390
Nitrogen	1.2507	799.5	28.080	22.450

The volume occupied by 1 mol of a gas at 0° and 76 cm. is 22.4 liters. Consequently the weight, p , of any given volume of gas, v , in liters, reduced to normal conditions is: $p = \frac{Mw. \times v}{22.4}$, and the volume, in liters, of any given weight of gas is: $v = \frac{22.4 p}{Mw}$.

When considering molecular quantities of gases the equation of

the general gas law: $vp = \frac{p_0 v_0}{273} T$ (p. 24) may be written: $vp = RT$, in which R is a constant, depending upon the units chosen, but not upon the nature of the gas. As 1 mol of a gas occupies 22.4 liters at 0° and 1 atm. pressure, if it be compressed to the volume of one liter at 0° , the value of p_0 would become 22.4 atm., and that of $v_0 = 1$. The value of $R = \frac{p_0 v_0}{273}$ would then be $\frac{22.4 \times 1}{273} = .0821$, and $vp = .0821T$; (vp = liter:atm.), a formula which is used in many calculations, e. g., $v = \frac{.0821T}{p}$, and $p = \frac{.0821T}{v}$.

Unsaturated vapors behave like gases (p. 30), and one mol of the unsaturated vapor of any substance therefore occupies 22.4 liters at 0° and 1 atm., or exerts a pressure of 22.4 atm. at 0° if compressed to the volume of 1 liter. The hypothesis that the unsaturated vapor of a substance which cannot be vaporized without decomposition would obey the same laws if it could exist is borne out by facts. From the formula: $p = \frac{.0821T}{v}$ the pressure, p , may be calculated for a mol of any substance, presuming its volume to be compressed or expanded. Thus, if we imagine 1 gm. of the hypothetical vapor of cane-sugar to occupy a volume of 100 cc. at 15.5° , a condition which would correspond to that existing in a 1 per cent solution of sugar, the volume which would be occupied by 1 mol ($C_{12}H_{22}O_{11} = 342$) would be 342×100 , or, 34.2 liters. Then the equation $p = \frac{.0821T}{v}$ would become $p = \frac{.0821 \times 288.5}{34.2} = 0.692$ atm. This value corresponds quite closely to the observed osmotic pressure, 0.684 atm., of a 1 per cent solution of sugar at the same temperature (see p. 70).

The molecular volumes of liquids and of their saturated vapors vary with the composition of the substance, and bear fixed relations to their critical temperature, pressure and density (p. 29).

The **Molecular Heat** of a substance is the product of its specific heat (p. 33) and its molecular weight. For solids the molecular heat is equal to the sum of the atomic heats (p. 55) of the elements contained in the molecule. Thus the atomic heat of hydrogen is 2.3, and that of oxygen is 4.0, from which the calculated molecular heat of ice is $2.3 \times 2 + 4 = 8.6$, while the observed specific heat of ice is 0.474, and $0.474 \times 18.016 = 8.54$.

The molecular heats of gases at constant pressure (p. 33) diminish with diminishing temperature, and appear to converge towards 6.3 at the absolute zero.

The **Molecular Heat of Vaporization** of a liquid is the amount of heat, expressed in calories, required to convert 1 mol of the substance into vapor at the same temperature as the liquid (p. 33), and is the

product of the heat of vaporization and the molecular weight. Thus for water at 100° it is $535.9 \times 18.016 = 9,654.8$ cal. The quotient obtained by dividing the molecular heat of vaporization by the absolute boiling point is approximately constant at 22. Thus for water: $9654.8 \div 373 = 25.8$. This value is departed from widely by substances whose molecular structure differs in the liquid and gaseous states.

Valence or atomicity.—It is known that the atoms of different elements possess different powers of combining with and of replacing atoms of hydrogen. Thus:

- 1 atom of chlorine combines with 1 atom of hydrogen.
- 1 atom of oxygen combines with 2 atoms of hydrogen.
- 1 atom of nitrogen combines with 3 atoms of hydrogen.
- 1 atom of carbon combines with 4 atoms of hydrogen.

The valence, atomicity, or equivalence of an element is the saturating power of one of its atoms as compared with that of one atom of hydrogen.

Elements may be classified according to their valence into—

Univalent elements, or monads	Cl'
Bivalent elements, or dyads	O''
Trivalent elements, or triads	B'''
Quadrivalent elements, or tetrads	Civ
Quinivalent elements, or pentads	Pv
Sexvalent elements, or hexads	Wvi

Elements of even valence, i. e., those which are bivalent, quadrivalent, or sexvalent, are sometimes called **artiads**; those of uneven valence being designated as **perissads**.

In notation the valence is indicated, as above, by signs placed to the right and above the symbol of the element.

But the valence of the elements is not fixed and invariable. Thus, while chlorine and iodine each combine with hydrogen, atom for atom, and in those compounds are consequently univalent, they unite with each other to form two compounds—one containing one atom of iodine and one of chlorine, the other containing one atom of iodine and three of chlorine. Chlorine being univalent, iodine is obviously trivalent in the second of these compounds. Again, phosphorus forms two chlorides, one containing three, the other five atoms of chlorine to one of phosphorus.

In view of these facts, we must consider either: 1, That the valence of an element is that which it exhibits in its most saturated compounds, as phosphorus in the pentachloride, and that the lower compounds are non-saturated, and have free valences; or 2, that the valence is variable. The first supposition depends too much

upon the chances of discovery of compounds in which the element has a higher valence than that which might be considered the maximum to-day. The second supposition — notwithstanding the fact that, if we admit the possibility of two distinct valences, we must also admit the possibility of others — is certainly the more tenable and the more natural. *In speaking, therefore, of the valence of an element, we must not consider it as an absolute quality of its atoms, but simply as their combining power in the particular class of compounds under consideration.* Indeed, compounds are known in whose molecules the atoms of one element exhibit two distinct valences. Thus, ammonium cyanate contains two atoms of nitrogen: one in the ammonium group is quinquivalent, one in the acid radical is trivalent.

When an element exhibits different valences, these differ from each other by two. Thus, phosphorus is trivalent or quinquivalent; platinum is bivalent or quadrivalent.

The chemical equivalent, or equivalent weight, of an element is the weight of that element capable of combining with unit weight of hydrogen (or chlorin). It is, therefore, its atomic weight divided by its valence. We have seen (p. 53) that 35.5 parts by weight of chlorin combine with 1 part by weight of hydrogen, 16 of oxygen with 2 of hydrogen, and 14 of nitrogen with 3 of hydrogen. Chlorin being univalent, oxygen bivalent and nitrogen trivalent, their equivalent weights are, therefore, respectively: $35.5 \div 1 = 35.5$, $16 \div 2 = 8$, and $14 \div 3 = 4.67$. (See also p. 64.)

A **gram-equivalent** (gm.:eq.) of an element is a quantity of that element whose weight in grams is equal to its molecular weight divided by its valence. Thus 23.05 gms. of sodium, and $65.4 \div 2 = 32.7$ gms. of zinc, are gram equivalents of those metals.

Symbols, Formulæ, Equations.—**Symbols** are conventional abbreviations of the names of the elements, whose purpose it is to introduce simplicity and exactness into descriptions of chemical actions. They consist of the initial letter of the Latin name of the element, to which is usually added one of the other letters. If there be more than two elements whose names begin with the same letter, the single-letter symbol is reserved for the commonest element. Thus, we have ten elements whose names begin with C; of these the commonest is Carbon, whose symbol is C; the others have double-letter symbols, as Chlorin, Cl; Cobalt, Co; Copper, Cu (Cuprum), etc.

These symbols do not indicate simply an indeterminate quantity, but represent one atom of the corresponding element.

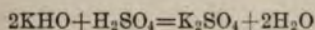
When more than one atom is spoken of, the number of atoms which it is desired to indicate is written either before the symbol or, in small figures, after and below it. Thus, H indicates one

atom of hydrogen; 2Cl , two atoms of chlorine; C_4 , four atoms of carbon, etc.

What the symbol is to the element, the **formula** is to the compound. By it the number and kind of atoms of which the molecule of a substance is made up are indicated. The simplest kind of formulæ are what are known as **empirical formulæ**, which indicate only the kind and number of atoms which form the compound. Thus, HCl indicates a molecule composed of one atom of hydrogen united with one atom of chlorine; $5\text{H}_2\text{O}$, five molecules, each composed of two atoms of hydrogen and one atom of oxygen, the number of molecules being indicated by the proper numeral placed before the formula, in which place it applies to all the symbols following it. Sometimes it is desired that a numeral shall apply to a part of the symbols only, in which case they are enclosed in parentheses; thus, $\text{Al}_2(\text{SO}_4)_3$ means twice Al and three times SO_4 .

For other varieties of formulæ, see pp. 85, 86.

Equations are combinations of formulæ and algebraic signs so arranged as to indicate a chemical reaction and its results. The signs used are the plus and equality signs; the former being equivalent to "and," and the second meaning "have reacted upon each other and have produced." The substances entering into the reaction are placed before the equality sign, and the products of the reaction after it; thus, the equation



means, when translated into ordinary language: two molecules of potash, each composed of one atom of potassium, one atom of hydrogen, and one atom of oxygen, *and* one molecule of sulfuric acid, composed of two atoms of hydrogen, one atom of sulfur, and four atoms of oxygen, *have reacted upon each other and have produced* one molecule of potassium sulfate, composed of two atoms of potassium, one atom of sulfur, and four atoms of oxygen, *and* two molecules of water, each composed of two atoms of hydrogen and one atom of oxygen.

As no material is ever lost or created in a reaction, the number of each kind of atom occurring before the equality sign in an equation must always be the same as that occurring after it. In writing equations, they should always be proved by examining whether the half of the equation before the equality sign contains the same number of each kind of atom as that after the equality sign. If it does not, the equation is incorrect.

The word "reaction" is used in chemistry with two distinct meanings: As applying to the action mentioned above, it refers to the mutual action of two substances upon each other. In the other

meaning it refers to the action of substances upon certain organic pigments. Thus, the reaction of a substance is **acid**, when it turns blue litmus red; **alkaline**, when it turns reddened litmus blue, and **neutral**, when it has no action upon either blue or red litmus.

Chemical reactions in the former sense are either: 1. **Combinations**, also called **syntheses**, in which elements or simpler compounds unite to form more complex molecules, as when $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$; 2. **Decompositions**, also called **analyses**, processes the reverse of combinations, as when $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2$; and 3. **Double decompositions**, or **matatheses**, when two substances mutually react upon each other with formation of new substances, as when $2\text{KHO} + \text{H}_2\text{SO}_4 = \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O}$. Special varieties of these several kinds of reaction, which are sufficiently distinctive, have received distinguishing names, such as condensations, etc., and will be considered later. There also occur, notably with the compounds of carbon, instances of **atomic rearrangement**, or **transposition**, in which the composition remains the same, but the constitution (p. 84) is changed: as when ammonium isocyanate, $\text{O}:\text{C}:\text{N}.\text{NH}_4$ is converted into urea, $\text{H}_2\text{N}.\text{CO}.\text{NH}_2$.

Electrolysis.—We have seen (p. 44) that when hydrochloric acid is electrolyzed, hydrogen is given off at the negative pole, and is therefore electropositive, while chlorin is given off at the positive pole, and is therefore electronegative. But if a compound of chlorin and sulfur be electrolyzed, chlorin is given off at the negative electrode, and is therefore electropositive. Chlorin is consequently electropositive to sulfur, and electronegative to hydrogen.

The results of electrolysis of binary compounds of many elements have shown that oxygen is electronegative, and the alkali metals (p. 215) are electropositive to all other elements with which they form binary compounds. If the elements be arranged in an **electrochemical series**, with oxygen at the electronegative end, and cesium at the electropositive end, and if the other elements be placed in the series in such positions that each will be between oxygen and all other elements toward which it is electronegative, it will be found that hydrogen will occupy a position about midway between the two ends, but nearer to the electronegative, and that the elements of the acidulous class (p. 101) will be placed between hydrogen and oxygen, while the metals will be placed to the electropositive side of hydrogen.

Arbitrarily, elements electronegative to hydrogen are considered as the electronegative elements, those electropositive to hydrogen as electropositive elements.

A similar separation takes place in the electrolysis of compounds containing more than two elements, one element being liberated at one pole and the remaining group of elements separating at the

other. This primary decomposition is generally modified, as to its final products, by subsequent chemical reactions, called **secondary actions**. When, for example, a solution of potassium sulfate is electrolyzed, the liquid surrounding the positive electrode becomes acid in reaction, and gives off oxygen. At the same time the liquid at the negative side becomes alkaline, and gives off a volume of hydrogen double that of the oxygen liberated. In the first place potassium sulfate, which consists of potassium, sulfur and oxygen, yields on primary separation electropositive potassium, which separates at the negative pole; and, an electronegative group of sulfur and oxygen, which goes to the positive pole: $2K_2SO_4 = 2K_2 + 2SO_4$. The potassium liberated immediately decomposes the surrounding water, forming caustic potash, to which the alkaline reaction is due, and hydrogen, which is liberated: $2K_2 + 4H_2O = 4KHO + 2H_2$. The sulfur-oxygen group at the positive pole also immediately reacts with water to form sulfuric acid, and oxygen is liberated: $2SO_4 + 2H_2O = 2H_2SO_4 + O_2$; one molecule of oxygen being liberated for every two of hydrogen. (See p. 70.)

In the electrolysis of an oxacid (below) that group which is primarily separated at the positive electrode is called the **residue** of the acid. (See p. 84.)

Acids, Bases and Salts.—All ternary and quaternary mineral substances have one of three functions. The function of a substance is its chemical character and relationship, and indicates certain general properties, reactions and decompositions which all substances having the same function possess and undergo alike. Function corresponds to the "family" of zoölogical and other scientific classifications, as lesser groups of the same function correspond to the "genera," and individual chemical substances to the "species." Thus in mineral chemistry we have **acids, bases and salts**; and in organic chemistry alcohols, aldehydes, acids, esters, etc.

An acid is a compound of an electronegative element or residue with hydrogen, which hydrogen it can part with in exchange for an electropositive element, without formation of a base. An acid has also been defined as a compound body which evolves water by its action upon pure caustic soda or potash. This latter definition is undesirable in view of the existence of certain zinc and aluminium compounds (pp. 240, 245) No substance which does not contain hydrogen can, therefore, be called an acid. (For other definitions of acids, bases and salts, see p. 77.)

The basicity of an acid is the number of replaceable hydrogen atoms in its molecule.

A **monobasic** acid is one containing a single replaceable atom of hydrogen, as nitric acid, HNO_3 : a **dibasic** acid is one containing two

such replaceable atoms, as sulfuric acid, H_2SO_4 ; a **tribasic acid** is one containing three replaceable hydrogen atoms, as phosphoric acid, H_3PO_4 . **Polybasic acids** are such as contain more than one atom of replaceable hydrogen.

Hydracids are acids containing no oxygen; **oxacids** or **oxyacids** contain both hydrogen and oxygen.

The term **base** is regarded by many authors as applicable to any compound body capable of neutralizing an acid. It is, however, more consistent with modern views to limit the application of the name to *such ternary compound substances as are capable of entering into double decomposition with acids to form salts and water*. They may be considered as one or more molecules of water in which one-half of the hydrogen has been replaced by an electropositive element or radical; or as compounds of such elements or radicals with one or more groups, OH. Being thus considered as derivable from water, they are also known as **hydroxids**. They have the general formula, $\text{M}_n(\text{OH})_n$. They are **monatomic**, **diatomic**, **triatomic**, etc., according as they contain one, two, three, etc., groups **oxhydroxyl**, or **hydroxyl** (OH). As acids having one, two or three, etc., atoms of replaceable hydrogen are designated as monobasic, dibasic, or tribasic acids, etc., so bases having one replaceable hydroxyl are spoken of as **monacid bases**, those having two as **diacid bases**, etc.

The atomicity of a compound is the number of hydroxyls in its molecule, which it may lose by their combination with the hydrogen of acids. Bases are said to be **monatomic**, **monohydric** or **monacid**; **diatomic**, **dihydric** or **diacid**, etc., according as the number of their hydroxyls is one, two, etc.

Thiobases, or **hydrosulfids**, are compounds in all respects resembling the bases, except that in them the oxygen is replaced by sulfur.

An **equivalent** of an acid or base is a quantity thereof equal to one molecule, divided by the basicity or acidity; or that proportionate quantity of its molecular weight which contains only one basic hydrogen atom or only one acid displaceable hydroxyl. Thus, a molecule and an equivalent of caustic potash, KHO, both weigh 56.16; a molecule of sulfuric acid, H_2SO_4 , weighs 98.08, and an equivalent 49.04.

A **gram-equivalent** (gm: eq.) of any substance is a quantity thereof whose weight is that of its equivalent, expressed in grams.

Equivalents and gram-equivalents of ions (p. 72) are quantities thereof corresponding to the same values of elements or compounds.

Concentration.—By the "concentration" or "strength" of a solution is understood the amount of the solute in unit volume of the

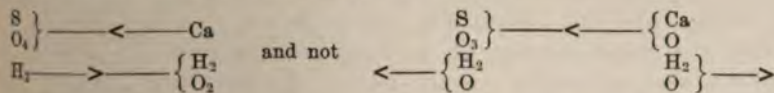
solution (not of the solvent). Various units are used for the expression of concentration:

In **percentage solutions**, strictly, both solvent and solute are taken in parts by weight. Thus, a 4 per cent solution of sodium chlorid is made with 4 gms. NaCl and 96 gms. H₂O. Volume: per cent solutions are usually more convenient: A 4 per cent solution of sodium chlorid is made by dissolving 4 gms. NaCl in a volume of water such that the finished solution measures 100 cc. The difference between per cent and v per cent solutions is more marked with solvents other than water. While per cent solutions are independent of temperature, v per cent solutions have the concentration indicated only at the temperature for which they are made, which is usually 18°C.

Normal solutions are of two kinds: **Molecular-normal**, which contain one gram-molecule in a liter of solution, and **Equivalent-normal**, which contain one gram-equivalent in a liter. Thus, one liter of M-N solution of sulfuric acid contains 98.08 gms. H₂SO₄, and one liter of Eq-N solution 49.04 gms. Usually "normal" solutions are molecular-normal, except solutions used in volumetric analysis, which are equivalent-normal, whole or fractional. **Decinormal solutions** ($\frac{N}{10}$) contain $\frac{1}{10}$ gm:mol. or gm:eq. per liter, etc. **Standard solutions** are solutions of some fixed volume-concentration, which may be of any value desired for the use intended.

A theoretical measure of concentration, frequently used in electrolytic calculations, and designated by the symbol η , is in gram-equivalents in one cc., although this degree of concentration very frequently cannot be actually attained.

Salts are substances formed by the substitution of electropositive, or basylous, elements for a part or all of the replaceable hydrogen of acids. They are formed, therefore, when bases and acids enter into double decomposition. They are not, as was formerly supposed, formed by the union of a metallic with a non-metallic oxid, but, as stated above, by the substitution of one or more atoms of an element or radical for the hydrogen of the acid. Thus, the compound formed by the action of sulfuric acid upon slaked lime is not SO₃CaO, but CaSO₄, formed by the interchange of atoms:



it is, therefore, **calcium sulfate**, and not **sulfate of lime**.

As salts are produced by double decomposition between acids and bases, the latter play as much part in the formation of salts as do the former, and we may also consider the salts as *substances formed by*

the substitution of acid residues (p. 84) for a part or all of the hydroxyl of bases.

It will be seen from the above that in some salts the hydrogen of the acid is only partly replaced, as in baking soda: $\text{OC} \begin{smallmatrix} \text{ONa} \\ \text{OH} \end{smallmatrix}$. Such salts are called **bi salts** or **acid salts**. There exist, also, salts in which a portion of the hydroxyl of the bases is retained. Such salts are called **basic salts**, e. g., basic lead nitrate NO_3PbOH . (See p. 83.)

The term **salt**, as used at present, applies to the compounds formed by the substitution of a basylous element for the hydrogen of *any* acid; and indeed, as used by some authors, to the acids themselves, which are considered as salts of hydrogen. It is probable, however, that eventually the name will be limited to such compounds as correspond to acids whose molecules contain more than two elements. Indeed, from the earliest times of modern chemistry a distinction has been observed between the **haloid salts**, i. e., those the molecules of whose corresponding acids consist of hydrogen, united with one other element, on the one hand; and the **oxysalts**, the salts of the oxacids, i. e., those into whose composition oxygen enters, on the other hand. This distinction, however, has gradually fallen into the background, for the reason that the methods and conditions of formation of the two kinds of salts are usually the same *when the basylous element belongs to that class usually designated as metallic*.

There are, however, important differences between the two classes of compounds. There exist compounds of all of the elements corresponding to the hydracids, binary compounds of chlorine, bromine, iodine and sulfur. There is, on the other hand, a large class of elements the members of which are incapable of forming salts corresponding to the oxacids. No salt of an oxacid with any one of the elements usually classed as metalloids (excepting hydrogen) has been obtained.

Haloid salts may be formed by direct union of their constituent elements; oxysalts are never so produced.

Osmotic Pressure.—We have seen (p. 18) that if water be floated upon the surface of a solution of sugar, diffusion begins at once, and continues until the solution and the solvent constitute a sugar solution of uniform concentration throughout. If, in place of bringing the solution and the solvent into direct contact, they be separated by placing the sugar solution in a porous earthenware jar in which a Pfeffer's semi-permeable membrane (p. 19) has been formed, and which is closed and fitted with a manometer, and the jar be then immersed in water, the passage of the water will be unimpeded, while that of the sugar will be arrested. As the water passes in, but the sugar remains, the pressure in the jar increases to a definite point,

when it remains stationary. At this point the pressure exerted by the water which has entered is in equilibrium with that exerted by the sugar molecules in their endeavor to escape, and is the measure of the **osmotic pressure** of the solution. Solutions having the same osmotic pressure are said to be **isosmotic**.

This pressure follows laws similar to those which govern gas pressures (pp. 19-23): It increases with the concentration. With a 1 per cent solution of sugar it is 0.704 atm., with a 2 per cent solution, 1.337 atm., with a 4 per cent solution 2.739 atm., and with a 6 per cent solution 4.046 atm., the pressures increasing very nearly in the proportion 1:2:4:6. Therefore, *the osmotic pressure is proportionate to the concentration, or inversely proportionate to the volume in which a given quantity of the substance is dissolved*. This corresponds to the Boyle-Mariotte law of gases: $vp = \text{constant}$. Further, we have seen, pp. 19, 25, that at high pressures gases do not rigorously obey the Boyle-Mariotte law, and similarly, it has been found that the osmotic pressures of concentrated solutions (measured indirectly) vary in precisely the same manner from those calculated in obedience to the rule.

The osmotic pressure increases with rise of temperature. Thus, with a 1 per cent solution of sugar it is 0.664 atm., at 6.8° ; 0.684 atm. at 15.5° , and 0.716 atm. at 32° ; from which the pressure at 0° would be 0.65 atm. These values correspond very nearly to the formula: $P = 0.65 (1 + .00367 t)$, in which the temperature coefficient .00367 is the same as in the gas formula. Therefore, *osmotic pressure is proportionate to the absolute temperature*. That is, it obeys the Dalton-GayLussac law (p. 23), and consequently $vp = RT$, as in the general gas law (p. 24).

Further, if 342.22 gms., one gm:mol., of sugar be dissolved in 22.4 liters of water, the solution is one of 1.532 per cent, and, as the osmotic pressure of a 1 per cent solution is 0.65 atm. at 0° , that of the gm:mol. solution in 22.4 is one atm. (0.996). This corresponds with the fact that the pressure of a gm:mol. of gas occupying 22.4 liters is one atm. (p. 57). And it has been shown by indirect methods that solutions of other substances containing 1 gm:mol. in 22.4 liters exert an osmotic pressure of one atm. Therefore, equal molecules of different substances, when dissolved in equal volumes of a solvent, exert equal osmotic pressures. Or, in the words of Van't Hoff: *Isosmotic solutions contain the same number of molecules of dissolved substance in a given volume, at a given temperature, and the number is the same as in an equal volume of a perfect gas at the same temperature and pressure*. This is in conformity with the postulate of Avogadro (p. 52), and consequently, *the osmotic pressure is the same as the gas pressure would be if the solvent were removed, and the dis-*

solved substance occupied the same volume, in the gaseous state, at the same temperature.

Therefore, the osmotic pressure of a solution may be used to determine the molecular weight of the solute, in the same way that the density of a gas or vapor is used for that purpose. But the accurate determination of osmotic pressure is attended with experimental difficulties, and, therefore, the principle is applied in indirect methods. Two such are in common use, both based upon the principle that, as the osmotic pressure increases with the concentration, it tends to oppose any diminution of the volume of the dissolved substance, as gas pressure opposes the contraction of volume of a gas. When a solution is cooled, a point is reached when the solvent begins to separate as a solid, leaving the solute in the unfrozen solvent, thus diminishing the volume of the former, and, therefore, by virtue of increased osmotic pressure the freezing point of the solution is lower than that of the pure solvent (p. 29). On the other hand, contraction of the volume of the dissolved substance is produced by driving off the solvent by evaporation or by boiling, and here again the osmotic pressure opposes the concentration, and, therefore, the vapor pressure of a solution is lower at any given tempera-

ture than that of the pure solvent (p. 31), and the boiling point of the former is consequently higher than that of the latter (p. 32). The depression of the freezing point of a solution and the elevation of its boiling point are, therefore, measures of the osmotic pressure, and, indirectly, they afford the means of determining the molecular weight of the solute.

Before the discovery of the laws of osmotic pressures, it had been learned empirically that if the amount by which the freezing point of a solution containing a fixed quantity of the solute (1 gm. in 100 cc.) is lowered be multiplied by the molecular weight of the solute, a constant quantity is obtained for each solvent. This is known as the **Law of Raoult**, and is equivalent to the statement that *equimolecular quantities of different substances dissolved in a given solvent produce the same depression of the freezing point of the solution*. The constant above referred to is 18.5 for water, 39 for glacial acetic acid, and 50 for benzene as solvents.

The usual form of the apparatus used for the determination of molecular weights by this "cryos-

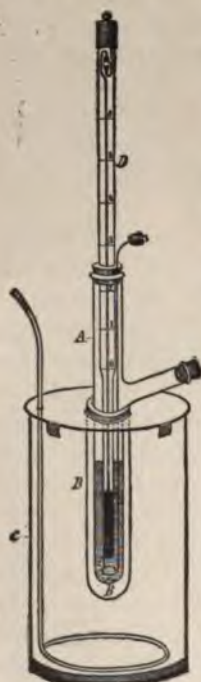


FIG. 23.

copie method" is shown in Fig. 23, in which A is the vessel containing the solvent, to which the solute is subsequently added through the lateral tube, and which also contains a wire stirrer. D is a very delicate (Beckmann) thermometer; and C is the vessel containing the cooling mixture, whose temperature should be about 5° below that of the solvent. The freezing point of the solvent is first accurately determined, and again after addition of a known weight of the substance. The molecular weight is obtained by the formula: $M = T \times \frac{p}{t}$; in which T is the constant for the solvent used, p the weight of the substance in solution, and t the observed depression of the freezing point in degrees centigrad. The difference between the freezing point of certain liquids and that of water is represented by the symbol Δ . Thus, for normal blood, $\Delta = -0.56^{\circ}$.

Molecular weights may also be determined from the depression of the vapor pressures of solutions; but, owing to experimental difficulties, the consequent elevation of the boiling points is resorted to in preference. The elevation of temperature is proportionate to the quantity of substance dissolved, if it be non-volatile. If molecular quantities be considered, equal elevations are observed with solutions containing equal gm:mols. of different substances in the same volume of solvent. And with different solvents the elevations are equal when the same quantity of substance is dissolved in equal gm:mols. of the several solvents.

For the determination of molecular weights from boiling point elevation, Beckmann's apparatus is customarily used. The boiling flask, A (Fig. 24) has a platinum wire fused into the bottom, and is partly filled with glass pearls and angular fragments of platinum (to ensure quiet boiling), and is surrounded by a glass steam jacket, B. Both A and B are fitted with return condensers, K_1 and K_2 , and the thermometer is fitted as shown in the figure. The boiling flask, with stoppers in both openings, is first weighed. The solvent is then introduced to the level shown, the stopper is replaced, and the flask and contents reweighed. The difference is the weight of solvent used. The apparatus is then mounted as shown in the figure, and the

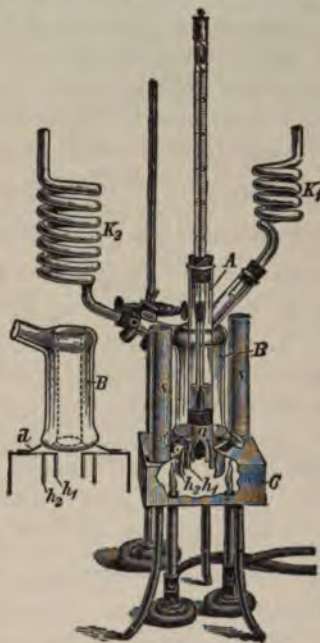


FIG. 24.

boiling point of the solvent is determined. A known weight of the substance is then introduced into the boiling flask, and the boiling point of the solution is determined. The molecular weight is obtained by the formula: $Mw = 100 c \cdot \frac{g}{G (t_1 - t)}$; in which Mw is the molecular weight; c , a constant called the "molecular elevation of boiling point of the solvent"; g , the weight of substance used; G , the weight of solvent used; t_1 , the boiling point after addition of the substance; and t , the boiling point of the solvent. The value of c is obtained from the heat of vaporization (p. 33) of the solvent, by the formula: $c = \frac{0.02 T^3}{h}$, in which T is the absolute boiling point of the solvent and h its heat of vaporization at its boiling point. Thus, for water: $c = \frac{0.02 \times (373)^3}{535.9} = 5.2$; for ethyl alcohol it is 11.5; for ether, 21.2; for acetic acid, 25.3; and for chloroform, 36.6.

As the osmotic pressure obeys the gas laws, and as the gas pressure may be calculated by the formula: $pt = (1 \times .00367t) p_0$ (p. 24), so the theoretical osmotic pressure may be obtained, in atmospheres, by the same formula, in which pt is the osmotic pressure at temperature t , and p_0 the osmotic pressure of a 1 per cent solution at 0° . The value of p_0 may be obtained from the molecular weight, as it is 1 atm. with a solution containing 1 gm:mol. in 22.4 liters, or $\frac{224}{M}$. Thus, for sugar $\frac{224}{342.22} = 0.6545$, and, if $t = 15.5^\circ$; $pt = 1.057 \times 0.6545 = 0.692$ atm. (See also p. 57.)

We have seen, p. 30, that when a liquid and its saturated vapor are in equilibrium, the vapor pressure of the liquid is balanced by the elastic force of the vapor; and that a similar equilibrium is established between a solid and its saturated vapor in sublimation (p. 32). Now when a solid is in contact with its unsaturated solution, the former diffuses through the latter until the solution becomes saturated (p. 28) at a given temperature. The process is then ended, and there is equilibrium between the osmotic pressure of the solution and that quality of the solid which corresponds to the vapor pressure of a liquid. This quality is called the **solution pressure** of the substance, and is equal to the osmotic pressure of its saturated solution.

As the kinetic theory of gases is based upon the phenomena expressed by the gas laws (p. 24), and as osmotic pressure obeys these laws, the kinetic theory of gases may also be applied to substances in solution, with possibly some modifications, which have, however, not been observed, due to collisions between the molecules of the solute with those of the solvent.

Electrolytic Dissociation—Ionization.—The observed osmotic

pressures of aqueous solutions of some substances agree very closely with those calculated from the gas law, but with other substances in aqueous solution the observed osmotic pressure is higher than that calculated, and the ratio of departure varies with different substances, and increases with the dilution of the solution. Those substances which follow the rule in the osmotic pressure of their aqueous solutions are not conductors of electricity, and are not electrolyzed by the galvanic current. Those which depart from the rule form solutions in which they are electrolyzed by the passage of the current, and which are conductors of the second order; the conductivity of the solution being the greater, the wider the departure from the rule in osmotic pressure. These facts formed the original foundation of the theory of electrolytic dissociation of Arrhenius, which is further strengthened by other facts.

The earlier researches of Faraday (1834) led to the discovery of the laws governing electrolysis which now bear his name. The first of these is the effect that *electrolysis does not occur unless the electrolyte is a conductor*.

If a current be passed through several voltmeters (Fig. 21, p. 45) of different resistances, and having electrodes of different metals, and differing in size, connected in series (p. 43) in the same circuit, the same volume of knall-gas will collect in each in the same time. This is in obedience to Faraday's second law, usually referred to as the first: *The energy of electrolytic action is the same in all parts of a circuit*.

If a number of vessels, fitted with platinum electrodes, and filled with solutions of salts of different metals, be connected in series in the same circuit, the weights of the several metals deposited upon the several cathodes will not be equal to each other. Thus, if in a given time the current deposits 107.93 mgms. of silver, in the same time it will have deposited 32.7 mgms. of zinc, 31.8 mgms. of copper, and 65.7 mgms. of gold from solutions of the salts of those metals. These are the proportions of the equivalent weights of the several metals: $\text{Ag} = \frac{107.93}{1} = 107.93$; $\text{Zn} = \frac{65.4}{2} = 32.7$; $\text{Cu} = \frac{63.6}{2} = 31.8$; and $\text{Au} = \frac{197.2}{3} = 65.7$. This is in accordance with the third law of Faraday, usually referred to as the second: *The amounts of different substances deposited by the same quantity of electricity are proportionate to their chemical equivalent weights*.

The **electrochemical equivalent** of a substance is the weight in grams of that substance separated by one coulomb of electricity, or by a current of one ampère in a second. Thus the electrochemical equivalent of hydrogen is 0.0001043, that of silver is 0.0011175, etc. (p. 45).

As one coulomb deposits 0.0011175 gm. of silver per second, it would require to deposit one gram-equivalent (107.93 gms.) per second $\frac{107.93}{0.0011175} = 96,581$ coulombs, or in round numbers 96,600 coulombs.

This quantity of electricity is called a **Faraday**, and, as the same quantity of electricity is required to deposit a gram-equivalent of any other substance, Faraday's laws may be summed up in the statement: *One Faraday, of 96,600 coulombs of electricity, is required to deposit one gram-equivalent of any substance.*

The name **ion** was first applied by Faraday to the primary products of electrolysis; and those which separate at the positive electrode, or anode, are called **anions**, while those which separate at the negative electrode, or cathode, are called **cations**. Thus, potassium sulfate yields the cation K, and the anion SO_4 . Cations are designated by the plus sign, anions by the minus sign. Thus: $\text{K}_2\text{SO}_4 = \overset{+}{\text{K}} \overset{+}{\text{K}} \overset{-}{\text{SO}_4}$, or, better, the cations, as well as their valences, are designated by the proper number of dots placed after the symbol, thus, $\text{H}^{\cdot}$, $\text{Ca}^{\cdot\cdot}$, and the anions similarly by prime marks, thus, OH' , SO_4'' , and AsO_4''' . *Hydrogen, the metals, and basic radicals are cations; hydroxyl and the acid residues are anions.*

According to the earlier views of electrolysis, the decomposition of the molecule into its ions was considered to be a result of the action of the galvanic current. According to the theory of Arrhenius, **dissociation** into ions, or **ionization**, occurs when the electrolyte is dissolved. A solution of potassium chlorid contains not only the molecular KCl, but also the cation K' and the anion Cl' , and the action of the current is to separate these, already liberated, ions at the respective electrodes. It is assumed that the hydrogen and metallic ions are charged with positive electricity, and the hydroxyl and acid-residue ions with negative electricity, and therefore (p. 39) the former are attracted to the negatively charged cathode, and the latter to the positively charged anode.

Notwithstanding the apparent violence of the assumption that a substance having such energetic action upon water as is shown by potassium (p. 222), can exist in aqueous solution, which assumption can only be reconciled with observed facts by the further supposition that in the ionic form potassium constitutes an allotropic modification (p. 17) differing from that in the atomic or molecular forms, the theory of electrolytic dissociation *on solution* is now generally accepted. Moreover, it not only offers reasons for the occurrence of certain observed facts, which it is difficult to explain otherwise, but is also of great service in the consideration of the reactions utilized in qualitative analysis.

We have seen that, according to the kinetic theory of gases

(p. 25), the particles of a gas are in constant motion, and that the pressure of the gas is proportionate to the number of impacts of the moving particles upon the walls of the containing vessel in unit time, and therefore to the rapidity of the motion (dependent upon temperature), and to the number of particles contained in unit volume. We have also seen (p. 67) that osmotic pressure obeys the same laws as gas pressure, and it may therefore be assumed that in a dilute solution the particles of the solute are in motion among the particles of the solvent in the same manner as are the particles of a gas, and that osmotic pressure is also proportionate to the number of particles in unit volume, and to the rapidity of the motion of the particles. We have already seen that osmotic pressure is proportionate to the concentration, and to the absolute temperature (p. 67). Therefore, if the osmotic pressure at constant temperature be greater than that corresponding to the concentration, i. e., the number of particles in unit volume, supposing the solute to be present in the molecular form, as we have seen (p. 71) is the case in solutions of electrolytes, but not in solutions of non-electrolytes, it follows that, while the solutions of the latter contain a number of particles equal to the number of introduced molecules, those of the former contain a greater number of particles. This would be the case if a solution of potassium chlorid, for example, contains not only the introduced molecules KCl , but also more or less of the dissociated ions K' and Cl' .

But the degree of departure from obedience to the law of osmotic pressure is not the same for all electrolytes, from which it may be inferred that *the degree of electrolytic dissociation in solution is not the same, other things being equal, with different electrolytes.*

If we express the concentration of a solution in gram:equivalents per cubic centimeter (p. 65) by η (the concentration in gram:equivalents per liter, equivalent-normal solution, would then be 1000η), and, assuming that dissociation is not complete, if we express the fraction which is dissociated by γ , then γ will be the **degree of dissociation**, i. e., the number of molecules dissociated, or the number of either anions or cations liberated. The **coefficient of dissociation** is the ratio of the dissociated molecules to the whole number of molecules introduced into the solution.

One method of determining the degree of dissociation is from the degree of departure from obedience to the law of osmotic pressure. The number of ions (n) formed on dissociation of a molecule depends upon the relative valences of the constituent atoms or groups. Thus, potassium chlorid, KCl , yields two ions, K' and Cl' ; zinc sulfate also two ions, Zn'' and SO_4'' ; potassium sulfate three ions, K' , K' and SO_4'' ; potassium phosphate four ions, K' , K' , K' and PO_4''' .

The ratio of $\frac{\text{observed osmotic pressure}}{\text{calculated osmotic pressure}}$ is known as **Van't Hoff's factor** and is designated by the symbol i ; whose value is equal to unity with non-electrolytes, and is less than unity with electrolytes. If each molecule yields two ions $i = 1 + \gamma$; if three ions $i = 1 + 2\gamma$, and if n ions $i = 1 + (n-1)\gamma$; from which $\gamma = \frac{i-1}{n-1}$. The value of γ , which would be unity with complete dissociation, approaches that value as dilution of the solution becomes greater. Thus, with potassium chlorid at a dilution of $1000\eta = 1.0$ the value of $\gamma = 0.748$; at $1000\eta = 0.1$, $\gamma = 0.853$; at $1000\eta = 0.01$, $\gamma = 0.934$; at $1000\eta = 0.001$, $\gamma = 0.973$; at $1000\eta = 0.0001$, $\gamma = 0.987$, and we may assume that at $1000\eta = \frac{1}{\infty}$, γ would $= 1.0$. Therefore, *the degree of dissociation increases with the dilution of the solution.*

The relation between conductance and electrolysis, no liquid being a conductor unless it be an electrolyte, nor an electrolyte unless it be a conductor, points to a causative relation between the two phenomena. The definite electrical relations of the ions to the electrodes, and the fact that ions are never separated from the liquid except at the electrodes, also point in the same direction, and all lead to the now generally accepted view that *the ions are the conductors of the current*, and that, becoming electrified in the manner above indicated, they are transferred by repulsion from one electrode, and attraction by the other, carrying their charges to the electrode whose polarity is opposite to their own. If this be true there must exist a relation between the conductivity (p. 42) of a solution and the degree of dissociation of the contained electrolyte: *the conductivity is directly proportionate to the number of free ions present.*

Taking as a unit of conductivity, κ , that of a body a column of which 1 cm. long and 1 cm.² in cross-section has a resistance of 1 ohm (p. 46), the conductivity of a body of the same magnitude having a resistance R will be: $\kappa = \frac{1}{R}$. The **equivalent conductivity** of an electrolyte in solution, designated by Λ , is the conductivity of a column 1 cm. long, and 1 cm.² in cross-section, containing 1 gm:eq. of the electrolyte in 1 cc., or $\Lambda = \frac{\kappa}{\eta}$. The **molecular conductivity**, designated by μ , differs from the equivalent conductivity in that the concentration of the solution is 1 mol per cc., in place of 1 gm:eq. per cc. Clearly the values of Λ and μ are the same when the equivalent and molecular weights are the same. The values of Λ as determined for potassium chlorid have been found to be: at $1000\eta = 1.0$, $\Lambda = 98.2$; at $1000\eta = 0.1$, $\Lambda = 111.9$; at $1000\eta = 0.01$, $\Lambda = 122.5$; at $1000\eta = 0.001$, $\Lambda = 127.6$; and at $1000\eta = 0.0001$, $\Lambda = 129.5$; from which it has been calculated that at $1000\eta = \frac{1}{\infty}$, Λ would $= 131.2$.

Therefore, *the equivalent conductivity increases proportionately with the dilution*; and we have here a second, independent means of determining the degree of dissociation. If we compare the value of Λ for $1000\eta = \frac{1}{\infty}$ obtained by this method with the values given above, by the factor $\frac{\Lambda}{\gamma}$, we obtain the very concordant values: 131.2, 131.1, 131.1, 131.1 and 131.2. Clearly, the value of γ can be calculated from that of Λ at any dilution by dividing the latter by its value for $1000\eta = \frac{1}{\infty}$.

The degree of dissociation is increased by elevation of temperature. The temperatures usually selected for determinations are 18° and 25° . At the same temperature and dilution the degree of dissociation varies greatly with different substances. The **dissociation constant** of a substance, designated by K , is the measure of its tendency to dissociation. If η represent the total concentration, i. e., the number of gm:eq. of a binary electrolyte in 1 cc., and γ the fraction thereof which is ionized, then $\gamma\eta$ is the number of anions, and the number of cations in 1 cc., and $\eta(1-\gamma)$ is the number of undissociated molecules.

From these values the dissociation constant is $K = \frac{(\gamma\eta)^2}{\eta(1-\gamma)}$. *The value of K is a measure of the chemical activity, or "strength" of a substance.* The conductivity of acids, and the influence of dilution thereupon, differ notably with different acids. Thus the values of Λ at the dilutions of $1000\eta = 1.0$; $1000\eta = 0.1$; $1000\eta = 0.01$, and $1000\eta = 0.001$ are respectively for hydrochloric acid: 301, 351, 370 and 377; for sulfuric acid: 198, 225, 308 and 361; and for acetic acid 1.32, 4.60, 14.03 and 41; showing that hydrochloric acid is highly ionized, even in the more concentrated solutions, sulfuric acid only becomes so on dilution, and the degree of ionization of acetic acid is small even at the higher dilutions. While certain chemical reactions, such as the solution of metals, the esterification of alcohols, and the hydrolysis of sugars are brought about by each of these acids, the time occupied in the reaction is the shortest with hydrochloric acid, and the longest with acetic acid. Therefore hydrochloric acid is the "strongest" of the three acids mentioned, and acetic acid is the "weakest"; *and the strength of an acid is proportionate to its degree of dissociation, i. e., to the number of free ions contained in its solution.* And the same is also true of bases.

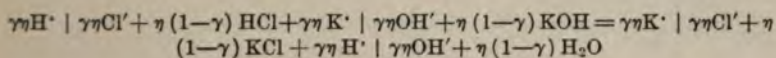
The variation of conductivity with dilution is also utilized to determine the basicity of acids. Almost all acids form soluble sodium salts. If the molecular conductivity of solutions of these be determined at a dilution of 1 mol in 32 liters, and again at a dilution of 1 mol in 1,024 liters, the increase in conductivity with dilution will be found to be very nearly constant with sodium salts of acids of like

basicity, but different with those of acids of varying basicity. The mean difference, represented by Δ , is: for monobasic acids $\Delta=1 \times 10.4=10.4$; for dibasic acids $\Delta=2 \times 9.5=19.0$; for tribasic acids $\Delta=3 \times 10.1=30.2$; for tetrabasic acids $\Delta=4 \times 10.3=41.1$, and for pentabasic acids $\Delta=5 \times 10=50.1$. This method is applicable in all cases except when the acid is so weak that its sodium salt is hydrolysed (p. 116) by water sufficiently to render the solution alkaline.

It is not to be inferred from what has been said above that, upon solution of an electrolyte, a certain proportion of the molecules are ionized and remain so, and that the remainder of the substance continues in its molecular condition; but rather that a condition of dynamic equilibrium is reached, similar to that between a liquid and its saturated vapor (p. 30), in which ionization and recombination of ions to molecules continue, the changes in one direction being equal to those in the other, so that their algebraic sum is zero. The ions are also assumed to be in constant motion, as are the molecules (p. 70), and liable to collision with each other, followed by their recombination. It is only when the ions come within the electric field between the electrodes that they acquire the continued motion toward their opposite electrodes under the influence of the electric charges. The degree of dissociation also remains constant for the existing temperature and dilution, notwithstanding the removal of ions by evolution of gases, deposition of metals, etc., until the extremely high dilution is reached when ionization is complete, and γ equals unity. Ions when thus separated at the electrodes either immediately resume the molecular condition, or enter into secondary reactions (p. 63).

We have seen that when an aqueous solution of an acid is electrolysed, hydrogen is always given off at the cathode. Although hydrogen exists in innumerable compounds other than acids, it is only from them that it is so separated, and only from them when in solution. That this hydrogen does not originate from the water is shown by the fact that perfectly pure water is neither a conductor nor an electrolyte. It is only in solutions of acids (or in solutions of acid salts or esters, which still retain acid properties), therefore, that hydrogen exists in the ionized form, as **hydrion**. Hydrion also differs from molecular or atomic hydrogen in other respects. It is only known in solution, while molecular hydrogen is almost insoluble in water. It reddens litmus and is replaceable by metals, properties not possessed by either atomic or molecular hydrogen. Similarly, when solutions of bases are electrolyzed hydroxyl, OH, is always produced as a primary product at the anode. And, here again, although hydroxyls exist in many compounds other than those having basic properties, it is only from solutions of these that hydroxyl is thus

separated, as only their solutions contain the ion, **hydroxidion**. And hydroxidion differs further from hydroxyl in that it is only known in solution, that it blues reddened litmus, and that it is replaceable by acid residues. Now, omitting the action of the galvanic current, and invoking the theory of Arrhenius that solutions of acids and bases contain the free ions, and remembering that ionization is not complete, we may write the equation representing the neutralization of an acid, hydrochloric, by a base, caustic potash, thus:



that is, the anion chloridion and the cation potassium unite to form potassium chlorid, while the cation hydron and the anion hydroxidion unite to form water; and, while the molecular acid and base are replaced by the molecular salt and water, the same kinds of ions are present after the neutralization as existed in the solution previous thereto.

Upon the facts above stated may be based definitions of acids, bases and salts, which are more concise than those given on pp. 63, 65.

An acid is a compound yielding hydron on electrolysis.

A base is a compound yielding hydroxidion on electrolysis.

A salt is a compound formed by the union of the anion of an acid and the cation of a base.

In the light, also, of the theory of electrolytic dissociation on solution, the language of the **laws of Berthollet**, which are generalized statements of facts which are the underlying principles of almost all of the reactions utilized in qualitative inorganic analysis, may be modified with advantage. These laws are usually thus stated:

1. *When solutions of two substances which can react with each other to produce a substance insoluble in the solvent are brought together, such insoluble substance is formed, and separates as a precipitate.*

2. *When solutions of two substances which can react with each other to produce a substance which is gaseous or volatile at the temperature of the reaction are brought together, such gaseous or volatile substance is produced, and escapes as a gas or vapor.*

The substances here under consideration are acids, bases and salts, which are electrolytes, and whose solutions therefore contain the free ions. When a solution of sodium chlorid is added to a solution of silver nitrate, the insoluble, and therefore, non-ionized silver chlorid separates, and the solution contains sodium nitrate: $\text{NaCl} + \text{AgNO}_3 = \text{AgCl} + \text{NaNO}_3$, or, from the point of view of ionization, the anion chloridion unites with the cation argention to form the insolu-

ble, molecular silver chlorid, and the solution, after the reaction, contains molecular sodium nitrate, along with sodion and nitrانى: $\text{Na} \cdot | \text{Cl}' + \text{Ag} \cdot | \text{NO}_3' = \text{AgCl} + \text{Na} \cdot | \text{NO}_3'$. This property of chloridion is manifested whatever may be the cation with which it is associated, whether it be hydrion or any metallic ion. It is, however, a property peculiar to chloridion, and is not manifested by chlorin in the molecular form or in any form of combination, whether molecular or ionic. Thus the reaction does not occur between solutions of silver nitrate and sodium chlorate, although the latter contains chlorin, because on solution it does not produce chloridion but the compound ion chlorانى: $\text{Na} \cdot | \text{ClO}_3'$. Similarly, when a solution of cupric sulfate and one of caustic potash are mixed, the cation cuprion and the anion hydroxidion unite to form the insoluble, molecular cupric hydroxid: $\text{Cu} \cdot \cdot | \text{SO}_4'' + 2\text{K} \cdot | \text{OH}' = \text{K}_2 \cdot \cdot | \text{SO}_4'' + \text{CuH}_2\text{O}_2$; and this reaction of cuprion is manifested whatever may be the anion with which it is associated. Again, when solutions of caustic potash and ammonium chlorid are brought together at a moderately elevated temperature, the unstable ammonium hydroxid which would otherwise result from the cation ammonion and the anion hydroxidion is decomposed to water and gaseous ammonia: $\text{K} \cdot | \text{OH}' + \text{NH}_4 \cdot | \text{Cl}' = \text{K} \cdot | \text{Cl}' + \text{NH}_4 \cdot | \text{OH}' = \text{K} \cdot | \text{Cl}' + \text{H}_2\text{O} + \text{NH}_3$. Therefore, *the properties of the ions are manifested irrespective of the nature of the ions of opposite polarity with which they are associated.*

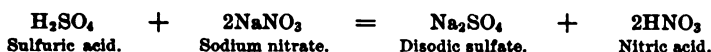
As solution is a necessary preliminary to the formation of precipitates, and as these are produced by the combination of ions whenever such union can produce a molecule insoluble in the solvent present, and as ions may be removed from solutions of electrolytes, not only by precipitation of insoluble products, but also by escape of gaseous or volatile products, the laws of Berthollet may be united in the statement: *When two ions may unite to form a molecule insoluble in the solvent, or gaseous or volatile at the existing temperature, such insoluble, gaseous, or volatile substance is produced and removed from the solution by precipitation or evolution.*

Stoichiometry ($\sigma\tau\omicron\chi\epsilon\acute{\iota}\omicron\nu$ = an element; $\mu\acute{\epsilon}\tau\rho\omicron\nu$ = a measure)—in its strict sense refers to the law of definite proportions, and to its applications. In a wider sense, the term applies to the mathematics of chemistry, to those mathematical calculations by which the quantitative relations of substances acting upon each other, and of the products of such reactions are determined.

A chemical reaction can always be expressed by an equation, which, as it represents not only the nature of the materials involved, but also the number of molecules of each, is a quantitative as well as a qualitative statement.

Let it be desired to determine how much sulfuric acid will be re-

quired to completely decompose 100 parts of sodium nitrate, and what will be the nature and quantities of the products of the decomposition. First the equation representing the reaction is constructed:



which shows that one molecule of sulfuric acid decomposes two molecules of sodium nitrate, with the formation of one molecule of sodium sulfate and two of nitric acid. The quantities of the different substances are, therefore, represented by their molecular weights, or some multiple thereof, which are in turn obtained by adding together the atomic weights of the constituent atoms:

$$\begin{array}{ccccccc} \text{H}_2\text{SO}_4 & + & 2\text{NaNO}_3 & = & \text{Na}_2\text{SO}_4 & + & 2\text{HNO}_3 \\ 1.01 \times 2 = 2.02 & 23.05 \times 1 = 23.05 & 23.05 \times 2 = 46.10 & 1.01 \times 1 = 1.01 \\ 32.06 \times 1 = 32.06 & 14.04 \times 1 = 14.04 & 32.06 \times 1 = 32.06 & 14.04 \times 1 = 14.04 \\ 16 \times 4 = 64.00 & 16 \times 3 = 48.00 & 16 \times 4 = 64.00 & 16 \times 3 = 48.00 \\ \hline 98.08 & & 85.09 \times 2 = 170.18 & 142.16 & & & 63.05 \times 2 = 126.10 \end{array}$$

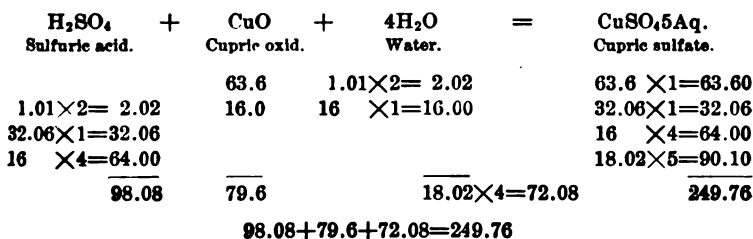
Consequently, 98.08 parts H_2SO_4 decompose 170.18 parts NaNO_3 , and produce 142.16 parts Na_2SO_4 , and 126.10 parts HNO_3 . To find the result as referred to 100 parts NaNO_3 , we apply the simple proportion:

$$\begin{array}{l} 170.18 : 100 :: 98.08 : 57.63 - 57.63 = \text{parts } \text{H}_2\text{SO}_4 \text{ required.} \\ 170.18 : 100 :: 142.16 : 83.53 - 83.53 = \text{ " } \text{Na}_2\text{SO}_4 \text{ produced.} \\ 170.18 : 100 :: 126.10 : 74.10 - 74.10 = \text{ " } \text{HNO}_3 \text{ " } \end{array}$$

As in writing equations (see p. 61), the work should always be proved by adding together the quantities on each side of the equality sign, which should equal each other: $98.08 + 170.18 = 268.26 = 142.16 + 126.10 = 268.26$, or $57.63 + 100 = 157.63 = 83.53 + 74.10 = 157.63$.

In determining quantities as above, regard must be had to the purity of the reagents used, and, if they be crystallized, to the amount of water of crystallization (see p. 17) they contain.

Let it be desired to determine how much crystallized cupric sulfate can be obtained from 100 parts of sulfuric acid of 92 per cent strength. As cupric sulfate crystallizes with five molecules of water of crystallization, the reaction occurs according to the equation:



98.08 parts of 100 per cent H_2SO_4 will produce, therefore, 249.76 parts of crystallized cupric sulfate. But as the acid liquid used contains only 92 parts of true H_2SO_4 , in 100; 100 parts of such acid will yield 234.27 parts of crystallized sulfate, for $98.08:92::249.76:234.27$.

In gravimetric quantitative analysis the substance whose quantity is to be determined is converted into an insoluble compound, which is then purified, dried and weighed, and from this weight the desired result is calculated.

Let the problem be to determine what percentage of silver is contained in a silver coin. Advantage is taken of the formation of the insoluble silver chlorid. A piece of the coin is chipped off and weighed: weight of coin used = 2.5643 grams. The chip is then dissolved in nitric acid, forming a solution of silver nitrate. From this solution the silver is precipitated as chlorid, by the addition of hydrochloric acid, according to the equation:

AgNO_3 Silver nitrate.	+	HCl Hydrochloric acid.	=	AgCl Silver chlorid.	+	HNO_3 Nitric acid.
$107.93 \times 1 = 107.93$		1.01		107.93		$1.01 \times 1 = 1.01$
$14.04 \times 1 = 14.04$		35.45		35.45		$14.04 \times 1 = 14.04$
$16 \times 3 = 48.00$						$16 \times 3 = 48.00$
169.97		36.46		143.38		63.05
$169.97 + 36.46 = 206.43 = 143.38 + 63.05$						

The silver chlorid is collected, dried and weighed:

Weight of coin used	2.5643 grams
Weight of AgCl obtained	3.0665 "

as 143.38 grams AgCl contain 107.93 grams Ag — $143.38:107.93::3.0665:2.3080$ — 2.5643 grams of the coin contain 2.3080 grams of silver, or 90 per cent — $2.5643:100::2.3080:90$.

Nomenclature.—The names* of the elements are mostly of Greek derivation, and have their origin in some prominent property of the substance. Thus, *phosphorus*, $\phi\omega\varsigma$, *light*, and $\phi\epsilon\rho\epsilon\upsilon$, *to bear*. Some are of Latin origin, as *silicon*, from *silex*, flint; some of Gothic origin, as *iron*, from *iarn*; and others are derived from modern languages, as *potassium* from *pot-ash*. Very little system has been followed in naming the elements, beyond applying the termination *ium* to the metals, and *in* or *on* to the non-metals; and even to this rule we find such exceptions as a metal called *manganese* and a non-metal called *sulfur*.

The names of *compound substances* were formerly chosen upon the

*For rules governing orthography and pronunciation of chemical terms, see Appendix A.

same system, or rather lack of system, as those of the elements. So long as the number of compounds with which the chemist had to deal remained small, the use of these fanciful appellations, conveying no more to the mind than perhaps some unimportant quality of the substances to which they applied, gave rise to comparatively little inconvenience. In these later days, however, when the number of compounds known to exist, or whose existence is shown by approved theory to be possible, is practically infinite, some systematic method of nomenclature has become absolutely necessary.

The principle of the system of nomenclature at present used is that the name shall convey the composition and character of the substance.

Compounds consisting of two elements, or of an element and a radical only, *binary compounds*, are designated by compound names made up of the name of the more electro-positive, followed by that of the more electro-negative, in which the termination *id* has been substituted for the termination *in*, *on*, *ogen*, *ygen*, *orus*, *ium*, and *ur*. For example: the compound of potassium and chlorine is called potassium chlorid, that of potassium and oxygen potassium oxid, that of potassium and phosphorus potassium phosphid.

In a few instances the older name of a compound is used in preference to the one which it should have under the above rule, for the reason that the substance is one which is typical of a number of other substances, and therefore deserving of exceptional prominence. Such are *ammonia*, NH_3 ; *water*, H_2O .

When, as frequently happens, two elements unite with each other to form more than one compound, these are usually distinguished from each other by prefixing to the name of the element varying in amount the Greek numeral corresponding to the number of atoms of that element, as compared with a *fixed* number of atoms of the other element.

Thus, in the series of compounds of nitrogen and oxygen, most of which contain two atoms of nitrogen, N_2 is the standard of comparison, and consequently the names are as follows:

N_2O	= Nitrogen monoxid.
NO ($=\text{N}_2\text{O}_2$)	= Nitrogen dioxid.
N_2O_3	= Nitrogen trioxid.
NO_2 ($=\text{N}_2\text{O}_4$)	= Nitrogen tetroxid.
N_2O_5	= Nitrogen pentoxid.

Another method of distinguishing two compounds of the same two elements consists in terminating the first word in *ous* in that compound which contains the less proportionate quantity of the more electro-negative element, and in *ic* in that containing the greater proportion; thus:

SO_2 = Sulfurous oxid.

SO_3 = Sulfuric oxid.

Hg_2Cl_2 (2Hg : 2Cl) = Mercurous chlorid.

HgCl_2 (2Hg : 4Cl) = Mercuric chlorid.

This method, although used to a certain extent in speaking of compounds composed of two elements of Class III (see p. 101), is used chiefly in speaking of binary compounds of elements of different classes.

In naming the *oxacids* the word *acid* is used, preceded by the name of the electro-negative element other than oxygen, to which a prefix or suffix is added to indicate the degree of oxidation. If there be only two, the least oxidized is designated by the suffix *ous*, and the more oxidized by the suffix *ic*, thus:

HNO_2 = Nitrous acid.

HNO_3 = Nitric acid.

If there be more than two acids, formed in regular series, the least oxidized is designated by the prefix *hypo* and the suffix *ous*; the next by the suffix *ous*; the next by the suffix *ic*; and the most highly oxidized by the prefix *per* and the suffix *ic*; thus:

HClO = Hypochlorous acid.

HClO_2 = Chlorous acid.

HClO_3 = Chloric acid.

HClO_4 = Perchloric acid.

Certain elements, such as sulfur and phosphorus, exist in acids which are derived from those formed in the regular way, and which are specially designated.

The names of the oxysalts are derived from those of the acids by dropping the word *acid*, changing the termination of the other word from *ous* into *ite*, or from *ic* into *ate*, and prefixing the name of the electro-positive element or radical; thus:

HNO_2
Nitrous acid.

HNO_3
Nitric acid.

HClO
Hypochlorous acid.

KNO_2
Potassium nitrite.

KNO_3
Potassium nitrate.

KClO
Potassium hypochlorite.

Acids whose molecules contain more than one atom of replaceable hydrogen are capable of forming more than one salt with electro-positive elements, or radicals, whose valence is less than the basicity of the acid. Ordinary phosphoric acid, for instance, contains in each molecule three atoms of basic hydrogen, and consequently is capable

of forming three salts by the replacement of one, two, or three of its hydrogen atoms, by one, two, or three atoms of a univalent metal. To distinguish these the Greek prefixes *mono*, *di*, and *tri* are used, the termination *ium* of the name of the metal being changed to *ic*, thus:

H_2KPO_4 = *Monopotassic phosphate*.

HK_2PO_4 = *Dipotassic phosphate*.

K_3PO_4 = *Tripotassic phosphate*.

The first is also called *dihydropotassic phosphate*, and the second, *hydropotassic phosphate*.

In the older works, salts in which the hydrogen has not been entirely displaced are sometimes called *bisalts* (bicarbonates), or *acid salts*; those in which the hydrogen has been entirely displaced being designated as *neutral salts*.

Some elements, such as mercury, copper, and iron, form two distinct series of salts. These are distinguished, in the same way as the acids, by the use of the suffix *ous* in the names of those containing the less proportion of the electro-negative group, and the suffix *ic* in those containing the greatest proportion, e. g.:

$(\text{Cu}_2)\text{SO}_4$ $(1\text{SO}_4 : 2\text{Cu})$ = *Cuprous sulfate*.

CuSO_4 $(2\text{SO}_4 : 2\text{Cu})$ = *Cupric sulfate*.

FeSO_4 $(2\text{SO}_4 : 2\text{Fe})$ = *Ferrous sulfate*.

$(\text{Fe}_2)(\text{SO}_4)_3$ $(3\text{SO}_4 : 2\text{Fe})$ = *Ferric sulfate*.

The names, *basic salts*, *subsals* and *oxysalts* have been applied indifferently to salts, such as the lead subacetates, which are compounds containing the normal acetate and the hydroxid or oxid of lead; and to salts such as the so-called bismuth subnitrate, which is a nitrate, not of bismuth, but of the univalent radical $(\text{Bi}'''\text{O}'')$.

By *double salts* are meant such as are formed by the substitution of different elements or radicals for two or more atoms of replaceable hydrogen of the acid, such as ammonio-magnesian phosphate, $\text{PO}_4\text{Mg}''(\text{NH}_4)'$.

In naming the cations, the termination *ion* is added to the stem of the name of the metal, the Latin name, if it exist, being used; but *sodion*, not *natrion*, and *potassion*, not *kalion*. Ionized hydrogen is called *hydrion*. The names of the anions are derived from those of the corresponding salts by changing the terminations from *id* to *idion*, e. g., S'' = *sulfidion*; *ite* to *osion*, e. g., SO_3'' = *sulfosion*; and *ate* to *anion*, e. g., SO_4 = *sulfanion*; except CO_3'' is called *carbanion*. The anion OH is called *hydroxidion*. When ions of different valence are derived from the same substance they are distinguished by the corresponding Greek numerals. Thus the electrolysis of H_2SO_4 proceeds in two stages, first $\text{H}_2\text{SO}_4 = \text{H}' \mid \text{HSO}_4'$ = *monosulfanion*, then $\text{HSO}_4' = \text{H}' \mid \text{SO}_4''$ = *disulfanion*.

Radicals.—Many compounds contain groups of atoms which pass from one compound to another, and, in many reactions, behave like elementary atoms. Such groups are called **radicals**, or **compound radicals**.

Marsh gas has the composition CH_4 . By acting upon it in suitable ways we can cause the atom of carbon, accompanied by three of the hydrogen atoms, to pass into a variety of other compounds, such as $(\text{CH}_3)\text{Cl}$, $(\text{CH}_3)\text{OH}$, $(\text{CH}_3)_2\text{O}$, $\text{C}_2\text{H}_3\text{O}_2$ (CH_3). Marsh gas, therefore, consists of the radical (CH_3) combined with an atom of hydrogen: $(\text{CH}_3)\text{H}$.

It is especially among the compounds of carbon that the existence of radicals comes into prominent notice. They, however, occur in inorganic substances also. Thus the nitric acid molecule consists of the radical NO_2 , combined with the group OH .

Like the elements, the radicals possess different valences, depending upon the number of unsatisfied valences which they contain. Thus the radical (CH_3) is univalent, because three of the four valences of the carbon atom are satisfied by atoms of hydrogen, leaving one free valence. The radical (PO) of phosphoric acid is trivalent, because two of the five valences of the phosphorus atom are satisfied by the two valences of the bivalent oxygen atom, leaving three free valences.

In notation the radicals are usually enclosed in brackets as above, to indicate their nature. The names of univalent radicals terminate in *yl* or in *gen*; thus: (CH_3) =methyl; (CN) =cyanogen.

The terms *radical* and *residue* are not synonymous. In speaking of acids their *radicals* are obtained by the subtraction of a number of hydroxyls equal to the basicity of the acid. Thus: $\text{HNO}_3 - \text{HO} = \text{NO}_2$; $\text{H}_2\text{SO}_4 - 2\text{HO} = \text{SO}_2$; $\text{H}_3\text{PO}_4 - 3\text{HO} = \text{PO}$. The *residue* is that which remains after removal of the basic, or replaceable, hydrogen. Thus: $\text{HNO}_3 - \text{H} = \text{NO}_3$; $\text{H}_2\text{SO}_4 - \text{H}_2 = \text{SO}_4$; $\text{H}_3\text{PO}_4 - \text{H}_3 = \text{PO}_4$. (See Electrolysis, p. 71.) The *anhydrids* (see p. 111) are derived from acids by removal of water. Thus: $2\text{HNO}_3 - \text{H}_2\text{O} = \text{N}_2\text{O}_5$; $\text{H}_2\text{SO}_4 - \text{H}_2\text{O} = \text{SO}_3$; $2\text{H}_3\text{PO}_4 - 3\text{H}_2\text{O} = \text{P}_2\text{O}_5$.

Composition and Constitution.—The characters of a compound depend not only upon the kind and number of its atoms, but also upon the manner in which they are attached to each other. There are, for instance, two substances, each having the empirical formula $\text{C}_2\text{H}_4\text{O}_2$, one of which is a strong acid, the other a neutral ester. As the molecule of each contains the same number and kind of atoms, the differences in their properties must be due to differences in the manner in which the atoms are linked together.

The composition of a compound is the number and kind of atoms contained in its molecule; and is shown by its empirical formula.

The constitution of a compound is the number and kind of atoms and their relations to each other, within its molecule; and is shown by its rational formula.

A rational formula is one which partly or completely indicates the constitution of the body. Rational formulæ are either **typical** or **graphic**. In the system of **typical formulæ** all substances are considered as being so constituted that their rational formulæ may be referred to one of three classes or **types**, or to a combination of two of these types. These three classes, being named after the most common substance occurring in each, are expressed thus:

The hydrogen type.	The Water type.	The ammonia type.
$\begin{array}{l} \text{H} \} \\ \text{H} \} \end{array}$	$\begin{array}{l} \text{H} \} \text{O} \\ \text{H} \} \end{array}$	$\begin{array}{l} \text{H} \} \\ \text{H} \} \text{N} \\ \text{H} \} \end{array}$
$\begin{array}{l} \text{H}_2 \} \\ \text{H}_2 \} \\ \text{etc.,} \end{array}$	$\begin{array}{l} \text{H}_2 \} \text{O}_2 \\ \text{H}_2 \} \\ \text{etc.,} \end{array}$	$\begin{array}{l} \text{H}_2 \} \\ \text{H}_2 \} \text{N}_2 \\ \text{H}_2 \} \\ \text{etc.,} \end{array}$

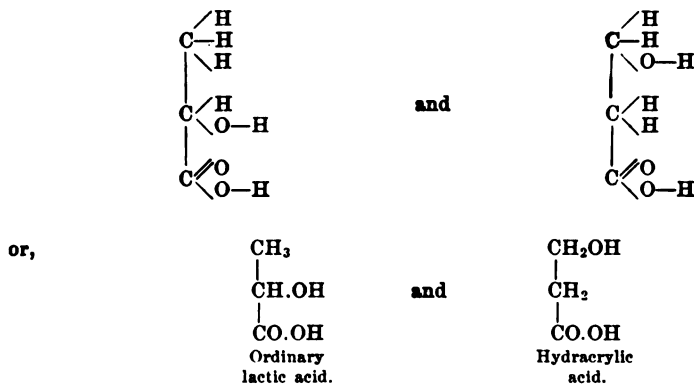
it being considered that the formula of any substance of known constitution can be indicated by substituting the proper element, or radical, for one or more of the atoms of the type, thus:

$\begin{array}{l} \text{Cl} \} \\ \text{H} \} \end{array}$	$\begin{array}{l} (\text{C}_2\text{H}_5)' \} \text{O} \\ \text{H} \} \end{array}$	$\begin{array}{l} (\text{C}_2\text{H}_5)' \} \text{N} \\ \text{H} \} \\ \text{H} \} \end{array}$	$\begin{array}{l} \text{Cl}_2 \} \\ \text{Ca} \} \end{array}$	$\begin{array}{l} (\text{SO}_2)'' \} \text{O}_2 \\ \text{H}_2 \} \end{array}$	$\begin{array}{l} (\text{CO})'' \} \text{N}_2 \\ \text{H}_2 \} \\ \text{H}_2 \} \end{array}$
Hydrochloric acid.	Alcohol.	Ethylamin.	Calcium chlorid.	Sulfuric acid.	Urea.

Typical formulæ are of great service in the classification of compound substances, as well as to indicate, to a certain degree, their nature and the method of the reactions into which they enter. Thus in the case of the two substances mentioned above, as both having the composition $\text{C}_2\text{H}_4\text{O}_2$, we find on examination that one contains the group $(\text{CH}_3)'$, while the other contains the group $(\text{C}_2\text{H}_3\text{O})'$. The difference in their constitution at once becomes apparent in their typical formulæ, $\begin{array}{l} (\text{CHO})' \} \text{O} \\ (\text{CH}_3)' \} \end{array}$ and $\begin{array}{l} (\text{C}_2\text{H}_3\text{O})' \} \text{O} \\ \text{H} \} \end{array}$, indicating differences in their properties, which we find upon experiment to exist. The first substance is neutral in reaction and possesses no acid properties; it closely resembles a salt of an acid having the formula $\begin{array}{l} (\text{CHO})' \} \text{O} \\ \text{H} \} \end{array}$. The second substance, on the other hand, has a strongly acid reaction, and markedly acid properties, as indicated by the oxidized radical and the extra-radical hydrogen. It is capable of forming salts by the substitution of an atom of a univalent, basylous element for its single replaceable atom of hydrogen: $\begin{array}{l} (\text{C}_2\text{H}_3\text{O})' \} \text{O} \\ \text{Na} \} \end{array}$.

Although typical formulæ have been and still are of great service, many cases arise, especially in treating of the more complex organic substances, in which they do not sufficiently indicate the relations between the atoms which constitute the molecule, and thus fail to convey a proper idea of the nature of the substance. Considering, for example, the ordinary lactic acid, we find its composition to be $C_3H_6O_3$, which, expressed typically, would be $(C_3H_4O)'' O_2$, a constitution supported by the fact that the radical $(C_3H_4O)''$ may be obtained in other compounds, as $(C_3H_4O)'' Cl_2$. This constitution, however, cannot be the true one, because in the first place, lactic acid is not dibasic, but monobasic; and in the second place, there is another acid, called hydracrylic acid, having an identical composition, yet differing in its products of decomposition. These differences in the properties of the two acids must be due to a different *arrangement* of atoms in their molecules, a view which is supported by the sources from which they are obtained and the nature of their products of decomposition.

To express the constitution of such bodies **graphic formulæ** are used, in which the position of each atom in relation to the others is set forth. The constitution of the two lactic acids would be expressed by graphic formulæ in this way:



Graphic formulæ are usually still further abbreviated, bonds being indicated by dots; thus: CH_3 . CHOH . COOH , and CH_2OH . CH_2 . COOH .

Chemical Energy—Affinity—Displacement—Stability.—Chemical energy frequently, but less properly, spoken of as **chemical force** or **chemism**, is that form of energy by which the atoms are held together in the molecule, and by which, under suitable physical con-

ditions, the attachments and arrangement of atoms are changed. It may be **potential**, i. e., latent, as in the molecules of carbon and oxygen, and capable of conversion into **kinetic**, or active energy, as in the manifestation of heat in their union to form carbon dioxid.

The atoms of different elements do not exhibit the same tendency to enter into combination with the atoms of a given element. Thus chlorin and oxygen readily combine with hydrogen, while the metals, except the alkaline metals and palladium, do not do so at all. Oxygen enters into combination with all of the other elements except fluorin and the elements of the argon group, while the last-named form no compound with any other element. Such differences in tendency to union were known to the alchemists, who referred to them as differences in the degree of affection or antagonism of the substances toward each other, and, as no cause is as yet known for the variations, beyond the surmise that they may be due to differences in electrical or other attraction, they are still referred to by saying that the elements have strong or weak **affinity**.

Frequently when an element is brought in contact with a compound the free element **displaces** one of those contained in the compound; as when chlorin is in contact with sodium iodid, sodium chlorid is formed and iodine liberated: $2\text{NaI} + \text{Cl}_2 = 2\text{NaCl} + \text{I}_2$. This is ascribed to the greater affinity of chlorin (p. 99).

There are also differences in the degree of permanence of compounds under the influence of slight variations in physical conditions. Thus, of the two compounds of hydrogen and oxygen, one, water, is dissociated only (p. 90) at very high temperatures, while the other, hydrogen peroxid, is decomposed by very slight heating. These variations are referred to by saying that certain compounds are **stable**, others **labile**, or **unstable**. The stability of the compound depends upon the affinities, the proportions, and the arrangement of the atoms in the molecule (p. 98).

Chemical Equilibrium.—When two or more substances are brought together, their association constitutes a **chemical system**. In this system an action may be set up, which will proceed to a certain point, and then cease. The system is then said to be in **chemical equilibrium**. As in mechanical, so in chemical equilibrium the condition of rest does not imply that no force is in action, but that the forces acting neutralize each other in such manner that their algebraic sum is zero; the condition is one of *dynamic equilibrium*.

As the "physical" conditions of concentration, pressure and temperature exert great influence upon the occurrence and extent of chemical changes, these must be taken into account along with affinity; and the "physical" phenomena of solution, and changes of

state of aggregation must also be considered along with changes of composition in the consideration of chemical equilibrium.

Equilibrium in a system all parts of which have the same physical properties and the same chemical composition (p. 49), as in a solution or in a mixture of liquids or of gases, is distinguished as **homogeneous equilibrium**; while **heterogeneous equilibrium** occurs in a system the parts of which are separated by bounding surfaces, as when solids and liquids, or immiscible liquids are in contact.

Distinction must also be made between **real** and **apparent** equilibrium. In a state of real equilibrium there is no change of relations, however slight or however slow, so long as the conditions of concentration, pressure and temperature remain constant, and changes which are caused by variations in these conditions take place regularly and continuously. Thus, in a system composed of a solution in contact with excess of the solute, variations in the proportions of the solute in the solution take place regularly with variations of temperature. Moreover, in this case the same condition of equilibrium is reached, whether it be approached from one side or from the other. Thus, a solution at a given temperature contains the same proportion of solute, whether it be obtained by addition to an unsaturated solution, or by deposition from a supersaturated solution. In a condition of apparent equilibrium it is probable that change is continuously taking place, although frequently with such extreme slowness that it escapes observation, even at constant concentration, temperature and pressure. Such changes as are caused by variations in these conditions in apparent equilibrium may, within certain limits, occur with regularity, but beyond these limits a sudden and more or less violent change takes place, after which the relations which existed previously are not restored by a return to the original conditions. Thus, in a system consisting of water and a mixture of hydrogen and oxygen, with moderate variation of temperature and pressure there are slight and regular variations in the amount of oxygen dissolved in the water, but at a certain elevation of temperature a sudden combination of the gases to form water takes place and, on cooling, the gases do not reappear.

The condition of chemical equilibrium is one corresponding to that of *stable* mechanical equilibrium, i. e., a condition to which the system tends to return when the equilibrium is disturbed. This general proposition is known as the **theorem of Le Chatelier**, and is thus expressed by Ostwald: *If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, i. e., one by which its effect is partly destroyed.*

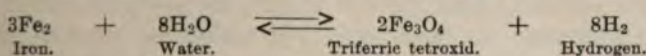
Thus, when the temperature of a system in equilibrium is raised,

that reaction takes place which is accompanied by absorption of heat (p. 97). and, conversely, when the temperature is lowered that reaction occurs which is accompanied by an evolution of heat. This is known as **Van't Hoff's law of movable equilibrium**.

When the pressure upon a system in equilibrium is increased, an action takes place which is accompanied by diminution in volume, and when the pressure is diminished, an action occurs which is attended with an increase in volume.

When the volume of a system in equilibrium is diminished, the pressure is increased, and an action occurs tending to relieve the pressure, and when the volume is increased the pressure is diminished, and an action takes place tending to raise the pressure.

Reversible Reactions.—Many reactions are known to occur in which displacements may be brought about in opposite directions. Clearly in these some influence other than affinity must determine in which direction the reaction will occur. Such are called **reversible reactions**, or **reversed actions**. Thus, if iron be heated in an atmosphere of vapor of water, the iron displaces the hydrogen of the water, which is liberated, and combines with the oxygen to form oxid of iron (p. 105). If, on the other hand, oxid of iron be heated in an atmosphere of hydrogen, the hydrogen displaces the iron, which is liberated, and combines with the oxygen to form water (p. 198). The reaction may take place, therefore, according to the following equation, read either from left to right, or from right to left:



If we start with pure iron and vapor of water the reaction will proceed according to the equation read from left to right until the proportion of hydrogen and water vapor present has reached a certain ratio, when the action will cease, and the system will be in equilibrium. Starting with pure oxid of iron and hydrogen, on the other hand, the reaction will proceed according to the equation read from right to left, and will cease when the ratio of hydrogen to water vapor will have acquired the same value as that reached in the first instance. As the condition of equilibrium reached in the two cases is the same when produced by proceeding in either direction, it is one of real equilibrium, and, as might be expected, if a mixture of iron and oxid of iron be heated in an atmosphere composed of hydrogen and water vapor in the proportion reached in either of the two former reactions, no change whatever will occur.

In any of the above experiments, mixtures of iron and oxid of iron in any proportions may be used without influencing the results in the slightest. The direction which the reaction will take to reach the

condition of equilibrium is, therefore, not determined by the relative amounts of the solid substances present, but by the ratio of the two gaseous constituents of the system. Moreover, for a given ratio of hydrogen to water vapor, the reaction will always proceed, if they be not in the ratio of equilibrium, in the same direction, whatever may be the weight or mass of either the gas or the vapor present. The direction of the reaction is, therefore, not determined by the *mass* of either the hydrogen or water vapor present, but by its *concentration*. And this explains why a solid, insoluble substance has no influence upon the direction which a reversible reaction will take. As solids vary in volume only slightly with variations of temperature and pressure, and as, when mixed, they form only mechanical mixtures (p. 47), which are heterogeneous, they do not vary in concentration; but gases and liquids, which form homogeneous, physical mixtures (p. 49), and whose volumes are notably modified by variations in pressure and temperature, also vary correspondingly in concentration, not only under the influence of those "physical" conditions, but also according to the proportions in which they are mixed.

Dissociation.—Vapor of water when heated at 1000° begins to decompose into its constituent elements, and the proportion of water decomposed increases with rise of temperature in such manner that at 2500° degrees half of the water present is split into a mixture of hydrogen and oxygen. This phenomenon, which is referred to as **dissociation**, is not peculiar to water vapor, and many other substances are similarly decomposed at more or less elevated temperatures, the extent of the decomposition increasing with elevation of temperature and with diminution of pressure. The reaction is also a reversible one; in the case of water $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$, and, on diminution of temperature or increase of pressure, recombination occurs in the sense of the equation read from right to left. Neither the decomposition nor the recombination occurs suddenly.

By dissociation the number of molecules in unit volume at constant volume is increased, therefore; at constant pressure the volume increases and the density diminishes. The extent of dissociation may be computed from the diminution of density at constant pressure.

Dissociation is in accordance with the kinetic theory of gases (p. 25). The velocity of motion of the molecules increases with rise of temperature, and the same cause produces increase of velocity of atomic motion within the molecule, until what may be termed the centrifugal energy of the atoms exceeds the chemical force of affinity, and the molecule is disrupted. But as the velocity of molecular and atomic motion of all the molecules present is not the same, some escape decomposition.

Velocity of Reaction.—Under given conditions of concentration,

temperature and pressure, every chemical reaction requires the lapse of a definite time for its completion. Usually this is short, but sometimes, as in atmospheric oxidations, quite extended, and sometimes, as in conditions of apparent equilibrium, too long for measurement.

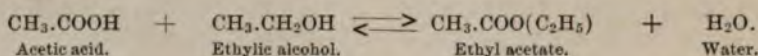
The time required for a given chemical reaction is always abbreviated by increase of temperature. Therefore, heat is applied to expedite a reaction; and to calm a too turbulent reaction it is conducted with artificial cooling. Although it is probable that in a system composed of two or more constituents capable of reacting with each other, such reaction occurs with varying degrees of slowness at all temperatures consistent with the maintenance of the gaseous or liquid state of aggregation, it frequently happens that it takes place with sensible rapidity only within certain ranges of temperature. This is true of many combinations and decompositions, and, notably, of the chemical processes occurring in living organisms. In a system composed of a large mass of material, the components of which unite with liberation of heat, the condition of apparent equilibrium is violently disturbed throughout the mass by the application of sufficient heat to start the reaction at a single point in the mixture; as when a mixture of hydrogen and oxygen is "exploded" by the passage of the electric spark.

Determinations of reaction velocity have been made principally with organic substances, in reactions which take place with sufficient slowness, and where the necessary conditions can be fulfilled. Clearly, from what precedes, such determinations must be made isothermally, i. e., at constant temperature, and the reactions selected must be irreversible, or nearly so.

From experiments with the inversion of cane-sugar (p. 318), a reaction which is irreversible, and progresses according to the equation: $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$, and the slow progress of which can be measured with the polariscope, it has been determined that *a constant fraction of the substance is decomposed during each unit of time, and that the velocity of reaction is proportionate to the concentration of the substance.*

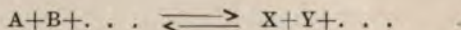
From this and other investigations it has been determined that for every reaction, at a given temperature and concentration, there is a definite **velocity constant**, which is designated by the symbol k . The value of k may be defined as the number of mols of a substance which are produced (or decomposed) in one minute by the interaction of (or with production of) one mol each of the constituents (or products), in a volume of one liter, in an apparatus so constructed as to be isothermal, and so that the substance or substances undergoing reaction may be maintained at constant concentration, and that the products of the reaction may be constantly removed.

Mass Action.—The example of a reversible reaction given above was one in a heterogeneous system, composed of solids and gases. As an example of a reaction of this kind occurring in a homogeneous system, a solution, we may consider that represented by the following equation:



If we start with ethyl alcohol and acetic acid, the reaction will proceed according to the equation, read from left to right; but if we start with ethyl acetate and water it will proceed from right to left. In neither case, however, will it be complete. If one mol each of the reacting substances have been used, real equilibrium will have been established and the reaction will have ceased when the composition of the mixture has become: $\frac{1}{3}$ mol acetic acid, $\frac{1}{3}$ mol alcohol, $\frac{2}{3}$ mol ethyl acetate and $\frac{2}{3}$ mol water. This statement is not to be taken as meaning that when this relation is attained no further action occurs, but that the changes in one direction have become equal in unit time to those in the opposite direction; the equilibrium being dynamic, not static.

If we designate any two or more substances bearing similar relations to each other to those between acetic acid and alcohol by $A+B+$. . . , and any two or more other substances, bearing the same relations to $A+B+$. . . as those which exist between acetic acid and alcohol on the one hand, and ethyl acetate and water on the other by $X+Y+$. . . , and supposing these to be contained in a homogeneous system, then the above equation may be expressed generally:



Invoking now the kinetic theory of gases as applied to solutions (pp. 25, 70): that the particles of $A+B+$. . . and $X+Y+$. . . , whether molecules or ions, are in constant motion, the activity of which is proportionate to the absolute temperature; at a given temperature the collisions between the particles $A+B+$. . . , and between $X+Y+$. . . will be the more numerous the greater the number of particles present in unit space, i. e., the greater the concentration. And assuming further that collisions between such particles are the prerequisite of their reaction with each other, it follows that the velocity of the reaction between $A+B+$. . . is proportionate to the product of their concentrations, and similarly with regard to the velocity of the reaction between $X+Y+$ Then if we express the concentration, in mols in a liter, of A, B, X, Y by C_a , C_b , C_x and C_y , the velocity of reaction, v , between

$A+B+$. . . will be $v=kC_aC_b$. . . , in which k is the velocity constant for the reaction and the temperature; and the velocity, v' , of the reaction between $X+Y+$. . . will be $v'=k'C_xC_y$. . . , in which k' is the velocity constant for this reaction and the same temperature. Neither the value of v , nor that of v' is observable in such a system, but the difference between them is, if any reaction occur. If no action takes place, then $v-v'=0$, or $v'-v=0$, and then kC_aC_b . . . $=k'C_xC_y$.

This is equivalent to the statement that: *When in a homogeneous system composed of reacting substances and their products of reaction at a given temperature, the product of the concentrations of the reacting substances and the velocity constant of their reaction is equal to the product of the concentrations of the products of reaction and the velocity constant of their reaction, the system is in real equilibrium, and no reaction occurs.*

But if any reaction do occur, its velocity, V , will be the difference between the velocities of any two possible reversible reactions, either $V=v-v'=kC_aC_b$. . . $-k'C_xC_y$. . . or $V=v'-v=k'C_xC_y$. . . $-kC_aC_b$. . . Which is equivalent to the statement that: *When the two products above referred to are not equal, a reaction occurs, which proceeds towards and to the establishment of such equality and equilibrium.*

The two italicized statements constitute the law of Guldberg and Waage, or the law of mass action, the latter rather a misnomer, as the direction of the action does not depend upon the relative masses, but upon the relative concentrations.

Heterogeneous Equilibrium — Phase Rule.—A heterogeneous system consists of two or more parts, each of which is homogeneous in itself but different, physically or chemically, from the other or others, the several parts being separated from each other by bounding surfaces. Such parts are called **phases** of the system, represented by the symbol P . As gases and vapors mix with each other in any proportions and constitute a homogeneous mixture, there can be but one gaseous phase in any system; and as a solution, whatever the number and amounts of the solutes, is also in itself homogeneous, any single liquid, either pure or acting as a solvent, can constitute but one phase of a system in equilibrium. But of immiscible liquids and solids a system may contain any number of phases. On the other hand, the same substance may constitute more than one phase of a system. Thus ice, water and vapor of water, being spacially distinct from each other, when together constitute a three-phase system.

The conditions of equilibrium in a system such as that last mentioned are three: concentration (volume), temperature and pressure. We have seen (p. 57) that equilibrium in a gas depends upon these

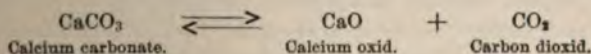
conditions, for by transposition of the equation $vp = RT$ we have $\frac{vp}{T} = R$, in which R is a constant. It has also been shown that the volumes of liquids and solids are modified by variations in temperature and pressure in the same manner as gases, although to a much less extent; therefore equilibrium in these depends upon the same conditions as that in gases. Now in the above equation the values of any two of the three variables v , p , and T may be fixed arbitrarily, but when they have been chosen the third is thereby made definite. This is expressed by saying that *a one-phase system, a gas, a liquid, or a solid, possesses two degrees of freedom*, represented by the symbol F . *The degrees of freedom of a system are the number of the variants, concentration, pressure and temperature which must be arbitrarily fixed in order that the condition of the system may be defined.* They are also expressed by saying that the system is *invariant, univariant, bivariant*, etc., according to their number. Clearly, the conditions of equilibrium in a one-phase system are those of homogeneous equilibrium. Heterogeneous equilibrium may exist only in systems containing two or more phases.

We have also seen that in a two-phase system, such as that made up of a liquid and its saturated vapor, only one of the three variables can be chosen arbitrarily, for (p. 31) if the temperature be arbitrarily fixed, any variation of the volume will be attended by evaporation or condensation, i. e., an action tending to restore the disturbed equilibrium, in such manner that the pressure remains constant, and a similar action will maintain a constant volume if the pressure be changed. Therefore a system composed of two phases of the same chemical substance has only one degree of freedom, and when that is chosen the other two become definite. It has also been shown that increase of pressure slightly diminishes the volume of liquid water, and at the same time correspondingly lowers the freezing point. Therefore the system ice:water also has but one degree of freedom. It can be stated in general terms that *the number of degrees of freedom diminishes with the increase of the number of phases present*. And if this be true, the addition of a third phase to the last system should produce one having no degree of freedom, and the system ice:water:vapor can only exist in equilibrium at one definite volume, pressure and temperature. This is found to be the case at a temperature of 0.0076°C . and a pressure of 4.6 mm. of mercury. This invariable point is the only one at which the three phases ice:water:vapor can exist in stable equilibrium together, and it is called the **triple point** of water. If the temperature be raised the ice disappears, and if it be lowered the water disappears. If the pressure be raised the vapor disappears, and if it be lowered the water disappears. Every sub-

stance has its triple point, near to, but not at, its fusing point. But the application of heat to the three-phase system ice:water:vapor at its triple point, or the withdrawal of heat therefrom, does not cause its immediate conversion into a two-phase system. If heat be added at constant volume it causes a portion of the ice to melt, i. e., $S \rightarrow L$ (solid to liquid), thereby becoming latent, without rise of temperature. But as the ice melts it contracts in volume, causing diminution of pressure, which brings about the passage of some ice to the form of vapor, $S \rightarrow V$, so that the sum of the effect of addition of heat is $S \rightarrow L + V$, and the abstraction of heat causes the reverse change, $L + V \rightarrow S$. Therefore, at temperatures above the triple point the solid cannot exist, and at temperatures below that point either system $S-L$ or $S-V$ may exist at first, and which of the two will remain on abstraction of heat at constant volume will depend upon the relative amounts of L and V present. With substances which expand on melting, which is the more usual case, the conditions are somewhat different. The addition of heat at the triple point causes the solid to melt, as in the former case, $S \rightarrow L$, but the solid expanding on fusion causes increase of pressure and condensation of vapor, i. e., $V \rightarrow L$, so that the sum of the first action of heat is $S + V \rightarrow L$; and whether the system finally resulting will be $S + L$ or $V + L$ depends upon the relative amounts of S and V present. In so far the condition of equilibrium is influenced by the relative masses of the phases present, but it is not otherwise influenced by either their absolute or relative masses. The withdrawal of heat causes the opposite changes.

If we start with the two-phase system water:vapor, and diminish the temperature, the latter will fall notably below that of the triple point, without the formation of the third phase, ice. This condition of superfusion (p. 29) is an instance of **suspended transformation**, which frequently occurs, the system being then in a condition of equilibrium which is designated as **metastable**. *A new phase is not formed immediately when the conditions of the system become such that its existence is possible, except it be already present.* Thus the metastable condition of superfused water is immediately converted into a condition of stable equilibrium, with rise of temperature and formation of ice, by contact with ice.

In the above we have considered equilibrium in a system all of whose phases have the same composition. When the several phases differ in composition, the question becomes more complex. Taking as an example the reversible reaction represented by the equation:



if we start with CaCO_3 at the ordinary temperature and pressure no reaction occurs, but on raising the temperature a reaction takes place according to the equation read from left to right until, at a definite temperature t_x , and a definite pressure p_x , the ratio between CaCO_3 and $\text{CaO} + \text{CO}_2$ has become fixed. Or, if we start from $\text{CaO} + \text{CO}_2$, then CaCO_3 will be formed, in the sense from right to left of the equation, until at t_x and p_x the same ratio between CaCO_3 and $\text{Ca} + \text{CO}_2$ is attained as in the first instance. The equilibrium is therefore real.

Let us suppose that the reaction has proceeded in either sense to t_x and p_x in a closed vessel, whose volume can be changed at will. The system will then be one of three phases, two solid and one gaseous. If now, maintaining t_x constant, the volume of the vessel be increased, a further change from left to right will occur, to such extent that p_x also remains constant, and if the volume be diminished at t_x , a reaction occurs from right to left, also to such extent that p_x remains constant. As t_x and p_x maintain their constant ratio for any arbitrarily chosen value of volume, the system is one of one degree of freedom, wherein it differs from the other three-phase system of ice:water:vapor, which is invariant.

The condition of equilibrium depends not only upon the number of phases present, but also upon the number of components. The **components** of a system are not all of the chemical species present, whether elements or compounds, but only such of these as can undergo independent variation of concentration in the several phases. Therefore, the elements constituting a compound are never considered as components of a system. In systems containing more than one component there is a certain degree of liberty in the selection of what substances shall be considered as components, but it is not the *nature*, but the *number* of components which is of importance, and this remains constant whatever the method of selection. The simplest method of determining the number of components is that suggested by Ostwald, which presupposes that the chemical composition of each phase present is known:

If each of all of the phases present, taken as a whole, has one and the same composition, the system contains one component or is of the first order. E.g., ice:water:vapor of water. If two phases must be mixed in suitable proportion, or combined, to obtain the composition of a third phase, the system contains two components, or is of the second order. E.g., $\text{CaCO}_3:\text{CaO}:\text{CO}_2$, in which $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$. And if three phases or constituents are necessary to obtain the composition of another phase, the system contains three components, or is of the third order. Such a system of two phases and three components is formed by shaking together chloroform (CHCl_3), water

(H_2O) and acetic acid ($\text{C}_2\text{H}_4\text{O}_2$). As CHCl_3 and H_2O are "immiscible," but each soluble in the other, on agitation and separation they form two layers, the upper 99.2 per cent H_2O and 0.8 per cent CHCl_3 , and the lower 99 per cent CHCl_3 and 1 per cent H_2O . If acetic acid, which is miscible in all proportions with both H_2O and CHCl_3 , be agitated with the above system, it is partitioned between the two layers, forming after separation, two liquid phases each containing H_2O , CHCl_3 and $\text{C}_2\text{H}_4\text{O}_2$ in different proportions.

Again comparing the two three-phase systems, ice:water:vapor and $\text{CaCO}_3:\text{CaO}:\text{CO}_2$, we have seen that the latter has one degree of freedom more than the former, and it also contains one more component. *The number of degrees of freedom in a system increases with the number of components.*

These relations are concisely and definitely expressed in the **Phase Rule of Gibbs:**

$$P + F = C + 2$$

or

$$F = C + 2 - P$$

in which P denotes the number of phases, F the number of degrees of freedom, and C the number of components. Thus, in the system, ice:water $P=2$, $C=1$. $F=1$; in that, ice:water:vapor, $P=3$, $C=1$. $F=0$; in that $\text{CaCO}_3:\text{CaO}:\text{CO}_2$, $P=3$, $C=2$. $F=1$; and in that $\text{CHCl}_3:\text{H}_2\text{O}:\text{C}_2\text{H}_4\text{O}_2$, $P=2$, $C=3$. $F=3$.

When the number of components reaches four there may be four degrees of freedom, as in the system $P=2$, $C=4$. $F=4$. This necessitates a greater number of variables than the three above mentioned. These independent variables are found in varying concentrations of the several components, or in the partial pressures of gaseous components.

Thermo-chemistry.—Thermodynamics is that branch of science which treats of the relations of heat to mechanical energy; thermo-chemistry has to do with the closely allied relations between heat and chemical energy. The two fundamental laws of thermodynamics are also applicable in thermo-chemistry:

1. *The apparent loss of energy in a closed system is always accompanied by the generation of an amount of heat which is exactly equivalent thereto.*

2. *Heat cannot pass of itself from a cold to a hot body, nor can it be so transferred without the expenditure of an equivalent amount of work.*

Chemical reactions, including "physical" solution, are always attended with a transformation of energy from potential to kinetic, or the reverse. The kinetic energy sometimes becomes manifest as electricity or light, but most frequently as heat. In some, **exothermic** reactions heat is generated, and in other, **endothermic** reactions heat

is absorbed from surrounding bodies, which are correspondingly cooled, and in both cases to a definite amount of heat per mol of substance, or substances, involved in the reaction. This definite amount of heat, measured in gram:calories or kilojoules (p. 22), is designated as positive (+) when heat is liberated in exothermic reactions, and as negative (—) when absorbed in endothermic reactions.

The act of solution is attended with a thermal effect, either positive or negative. The **heat of solution** of a substance is the amount of heat generated or absorbed in the solution of one gram of the substance in a large quantity of water. The heat of solution of gases and liquids is always positive. Thus, for chlorine it is +4290 cal., and for hydriodic acid +18630 cal.; for ethylic alcohol it is +2000 cal., and for sulfuric acid +17850 cal. The heat of solution of solids is sometimes positive, as +12500 for potassium hydroxid, but most frequently negative, as —1180 for sodium chlorid. The **heat of precipitation** of difficultly soluble solids is the negative value of their heat of solution, and is the greater the more difficultly soluble the substance is. Thus, for silver chlorid, bromid and iodid: +15800, +20200, and +26600 cal. respectively.

The heat measurable in a given chemical reaction is not entirely the result of the reaction itself, and is not, therefore, a measure of the "affinities" of the substances involved, but is the algebraic sum of a number of factors, some positive, others negative, of physical and chemical character: the energy required to split the molecule into atoms, the combination of the liberated atoms to form new molecules; the condensation of gases or vapors to liquids, the vaporization, solution or precipitation of products, the diminution of the number of molecules in unit volume, and the performance of external work.

Usually chemical combinations are exothermic, as when two molecules of hydrogen and one molecule of oxygen combine to form one molecule of water 136,800 gm:cal, or 572 *kJ* of heat are liberated. This is expressed by the equations: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} + 2 \times 68,400 \text{ cal}$, or $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} + 2 \times 286 \text{ kJ}$. But some combinations are endothermic, as when hydrogen and iodine combine to form hydriodic acid: $\text{H}_2 + \text{I}_2 = 2\text{HI} - 2 \times 6097 \text{ cal.} = -2 \times 25 \text{ kJ}$.

Exothermic reactions, once started, continue without the further addition of heat energy, sometimes violently, as in the case of $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$. Endothermic reactions require the continued supply of heat for their continuance. The greater the amount of heat generated in an exothermic reaction the more readily will it occur, and the more stable will be the product. Compounds whose formation is endothermic are formed with difficulty, and are less stable than a mixture of

their constituents, and therefore prone to decomposition. For this reason hydriodic acid is used in organic chemistry as a source of nascent hydrogen, as a reducing agent (p. 108). Compounds whose formation is exothermic are decomposed by the addition of sufficient heat, as in the dissociation of vapor of water and other vapors and gases (p. 90). The decomposition of compounds whose formation is endothermic is attended by evolution of heat, as in the decomposition of nitrates and chlorates. In such reactions any heat imparted from outside serves only to incite the decomposition.

The **heat of formation** of a compound is the heat effect, positive or negative, observed or calculated, attending the formation of one mol of the compound from its elements. Thus the heat of formation of water is +68,400 cal, that of hydriodic acid -6,097 cal.

The heat of formation of compounds, other than the heats of combustion, must usually be determined indirectly. Thus the heat of formation of hydrogen peroxid cannot be directly measured, but the heat effect of the formation of water from hydrogen and oxygen can be, as well as that of the decomposition of hydrogen peroxid to water and oxygen. The former is represented by the equation (1): $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} + 2 \times 68,400$ cal, and the latter by the equation (2): $2\text{H}_2\text{O} = 2\text{H}_2 + \text{O}_2 + 2 \times 68,400$ cal. Equation 2 may be transposed to read (3): $2\text{H}_2\text{O} + \text{O}_2 = 2\text{H}_2\text{O}_2 + 2 \times 23,193$ cal, and, adding together equations 1 and 3 we have: $2\text{H}_2 + 2\text{O}_2 = 2\text{H}_2\text{O}_2 + 2 \times 45,207$. The heat of formation of hydrogen peroxid is, therefore, 45,207 gm:cal, or 189 kj.

When a mol of a compound is decomposed, the heat effect is equal to its heat of formation, but of opposite sign.

The **heat of combustion** of a substance is the amount of heat liberated by the complete burning of one mol of the substance in an excess of pure oxygen under pressure. This value has been directly determined for a great number of organic substances, by burning known weights in a *calorimetric bomb*, contained in a *water-calorimeter*, where the heat generated is measured by the rise of the temperature of the known weight of water.

The **heat of reaction** is the heat effect, positive or negative, produced in any reaction. It is equal to the sum of the heats of formation of the substances produced, minus the sum of the heats of formation of the substances reacting. Thus the heat of formation of hydrobromic acid is 8,369 cal, and that of hydrochloric acid is 21,997 cal. The heat of reaction of $2\text{HBr} + \text{Cl}_2 = 2\text{HCl} + \text{Br}_2$ is, therefore, $2 \times (21,997 - 8,369) = 2 \times 13,628$. The heat of reaction may also be obtained from the heats of combustion, as the heat of reaction is equal to the sum of the heats of combustion of the reacting substances, minus the sum of the heats of combustion of those formed.

Thus the heats of combustion of acetic acid, ethylic alcohol, and ethyl acetate are respectively 2,100, 3,400 and 5,540 cal, and therefore the heat of the reaction $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{OH} = \text{CH}_3\text{COO}(\text{C}_2\text{H}_5) + \text{H}_2\text{O}$ is $(2,100 + 3,400) - (5,540 + 0) = -40$ cal.

As a rule, that reaction between several substances present in a system will occur which will result in the formation of the compound having the greatest heat of formation. Thus the heats of formation of the hydrogen compounds of the halogens are: for $\text{HF} + 38,495$ cal, for $\text{HCl} + 21,997$ cal, for $\text{HBr} + 8,369$ cal, and $\text{HI} - 6,097$ cal, which explains why reactions such as $2\text{HBr} + \text{Cl}_2 = 2\text{HCl} + \text{Br}_2$ occur. Yet these reactions do not proceed to completion; they are reversible to a certain extent in obedience to the law of mass action.

The heat of reaction between a given pair of substances is not the same at all temperatures of the reaction if the substances be gaseous or liquid. It varies with the specific heats of the substances involved in such manner that the excess of the molecular heats of the reacting substances over the molecular heats of the products represents the increase of the heat of reaction for each degree of temperature elevation. But as in solid substances the molecular heats are additive, i. e., the sum of the atomic heats, the heat of reaction between solid substances is independent of the temperature.

4. When solutions of salts are mixed there is no heat effect unless a precipitate or a volatile compound is formed, i. e., unless the ions unite to form an electrically neutral molecule. The heat effect produced by the union of two ions to form a neutral molecule is, of course, always the same for the same two kinds of ion, and, therefore, the **heat of neutralization** between strong acids and strong bases in dilute solution is a constant quantity, viz., 13,700 cal, provided they do not form precipitates, because the ionic reaction which is common to all is $\text{H}' + \text{OH}' = \text{H}_2\text{O}$, or $(\text{H}'\text{aq.}, \text{OH}'\text{aq.}) = 13,700$ cal, in which aq represents a large quantity of water. With weak acids or bases, which are less completely dissociated, the heat of neutralization is greater or less than 13,700 cal. Thus, with potassium or sodium hydroxid and acetic acid it is 13,400 cal, with the same bases and phosphoric acid it is 14,830 cal, and with ammonium hydroxid and hydrochloric acid it is 12,300 cal. The difference between these values and 13,700 cal is the **heat of dissociation** of the weak acid or base, which may be positive or negative: +300 cal for acetic acid, -1,130 cal for phosphoric acid, and +1,400 cal for ammonium hydroxid.

Classification of the Elements.—The elements are best classified according to resemblances in their chemical properties. We will adopt such a classification, based upon the nature of the oxids and the existence or nonexistence of oxysalts:

Class I. Typical Elements.**Hydrogen.****Oxygen.**

Although these two elements differ notably in their properties, they are here classed as *typical elements*, because together they form the basis of our classification; they both play important parts in the formation of acids; neither would find a suitable place elsewhere in the classification; and they may also be considered as typical from the point of view of ionization, as they form the characterizing ions of acids and bases, hydron and hydroxidion.

Class II.

Elements which form no compounds:

Helium, neon, argon, krypton, xenon.

Class III. Acidulous Elements.

Elements whose oxids unite with water to form acids, never to form bases. Which do not form oxysalts.

GROUP I.—Fluorin, chlorin, bromin, iodin.

GROUP II.—Sulfur, selenium, tellurium.

GROUP III.—Nitrogen, phosphorus, arsenic, antimony.

GROUP IV.—Boron.

GROUP V.—Carbon, silicon.

GROUP VI.—Vanadium, niobium, tantalum.

GROUP VII.—Molybdenum, tungsten, osmium.

Elements of this class are also called **non-metals**, in contradistinction to those of classes IV and V, which are collectively called **metals**. They are also referred to as **electronegative elements**, because they are electronegative to hydrogen, although they are all electropositive to oxygen, and individual members are also electropositive to others of the class (p. 62). On electrolysis of compounds containing acidulous elements or oxygen, and metals or hydrogen, the former are usually found in the anion, the latter in the cation, as $H'K' | SO_4''$. But this is not invariably the case. Thus, on electrolytic separation of a solution of sodium sulfantimonite elementary antimony is deposited at the cathode.

Class IV. Amphoteric Elements.

Elements whose oxids unite with water, some to form bases, other to form acids. Which form oxysalts.

GROUP I.—Gold.

GROUP II.—Chromium, manganese, iron.

GROUP III.—Radium, thorium, uranium.

GROUP IV.—Lead.

GROUP V.—Bismuth.

GROUP VI.—Titanium, germanium, zirconium, tin.

GROUP VII.—Palladium, platinum.

GROUP VIII.—Rhodium, ruthenium, iridium.

The amphoteric and basylous elements are the **metals or electro-positive elements**, and have these properties in common: they form oxysalts, and are separated as cations on electrolysis of such salts.

Class V. Basylous Elements.

Elements whose oxids unite with water to form bases, never to form acids. Which form oxysalts.

GROUP I.—Lithium, sodium, potassium, rubidium, cesium, silver.

GROUP II.—Thallium.

GROUP III.—Calcium, strontium, barium.

GROUP IV.—Magnesium, zinc, cadmium.

GROUP V.—Beryllium, aluminium, scandium, gallium, indium.

GROUP VI.—Nickel, cobalt.

GROUP VII.—Copper, mercury.

GROUP VIII.—Yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, thulium, ytterbium.

This class includes the more strongly electropositive metals.

In classes III, IV and V the elements are subdivided into groups, the members of which have common distinctive characters, and are more or less closely allied to each other. In classes III and V the resemblances between individuals of groups occurring first in the list are the most marked, and are more close than those between members of groups placed lower down.

Periodic Law.—If the elements be arranged in a continuous series in the numerical order of their atomic weights: H, He, Li, Be, etc., it will be found that elements having similar properties, in themselves and in their compounds, will be separated from each other by regular but increasing spaces or "periods." Thus the members of the group F, Cl, Br, I, will be separated by 7, 17, 17 spaces, and the members of the group Li, Na, K, Rb, Cs by 7, 7, 17, 17 spaces. If now these periods be arranged in parallel columns, as shown in the table on page 103 for example, it will be found that elements having similar properties will fall in the same (horizontal) line. It will be observed, however, that in order to attain this result it has been

	H 1.008	Li 7.08	Na 23.06	K 39.15	Rb 85.4	Cs 132.	
				Ca 40.1	Sr 87.6	Ba 137.4	Ra 226
						La 138	
						Ce 140	Th 232.5
						Pr 140.5	
						Nd 143.6	
						Sm 150.2	
						Eu 151.7	U 238.5
						Gd 156	
						Tb 160	
						Ho 162	
						Er 166	
						Tm 171	Ac ?
						Yb 173	
				Sc 44.1	Yt 89		
				Ti 48.1	Zr 90.7		
				V 51.2	Nb 94	Ta 183	
				Cr 52.1	Mo 96	W 184	
				Mn 55			
				Fe 55.9	Ru 101.7	Os 191	
				Co 59	Rh 103	Ir 193	
				Ni 58.7	Pd 106	Pr 194.8	
				Cu 63.6	Ag 107.93	Au 197.2	
	Be 9.1	Mg 24.36	Zn 65.4	Cd 112.4	Hg 200.3		
	B 11	Al 27.1	Ga 70	In 114	Tl 204.1		
	C 12	Si 28.4	Ge 72.5	Sn 118.5	Pb 206.9		
	N 14.04	P 31	As 75	Sb 120.2	Bi 208.5		
	O 16	S 32.06	Se 79.1	Te 127.6			
	F 19	Cl 35.45	Br 79.96	I 126.95			
	He 4	Ne 20	A 39.9	Kr 81.8	X 128		

necessary to reverse the order of three pairs of elements: A and K, Co and Ni, and Te and I; but with these alterations the periodicity of recurrence of related elements will be particularly noticeable by

comparing the first two and last four of the horizontal lines of the table with the previous classification of elements. This connection between the periodicity of the atomic weights of the elements and their chemical relationships is expressed in the **Periodic law** of Mendelejeff: *The properties of elements, the constitution of their compounds, and the properties of the latter are periodic functions of the atomic weights of the elements.* But the law is not absolute, and, apart from the necessity of transpositions to adapt it to the obvious relationships mentioned above, the separation into different groups of such closely related elements as Cu and Hg, Cr, Mn and Fe, and Co and Ni, and the grouping together of such dissimilar elements as Cu, Ag and Au are not in accordance with observed fact.

It will be observed that the series is complete, with but a single break, between $H = 1.008$ and $Nd = 143.6$, but that above that point the breaks are numerous. When the earlier tables were constructed (about 1870) the breaks were more numerous, but have been in part filled by the discovery of then unknown elements, such as scandium, germanium, and the entire argon group. It may, therefore, be expected that other breaks, still existing, may be filled by the discovery of other new elements of very high or very low atomic weights. In this connection it may be noted that there is some reason for the belief that a third element may exist between H and He, and that there may be another period of three elements, of lower atomic weights than that of hydrogen.

INORGANIC CHEMISTRY.

CLASS I.—TYPICAL ELEMENTS.

HYDROGEN — OXYGEN.

ALTHOUGH, in a strict sense, hydrogen is regarded by most chemists as the one and only type-element—that whose atom is the unit of atomic and molecular weights—the important part which oxygen plays in the formation of those compounds whose nature forms the basis of our classification, its acid-forming power in organic compounds, and the differences existing between its properties and those of the elements of the sulfur group, with which it is usually classed, warrant us in separating it from the other elements and elevating it to the position it here occupies.

HYDROGEN.

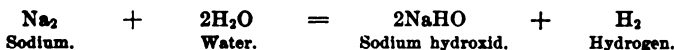
Symbol = H — Univalent — Atomic weight = 1 (1.008 — O = 16) — Molecular weight = 2 (2.016 — O = 32) — Sp. gr. = 0.06926A — One litre weighs 0.0899 gram — 100 cubic inches weigh 2.1496 grains — 1 gram measures 11.16 litres — 1 grain measures 46.73 cubic inches — Name derived from ὕδωρ = water, and γεννάω = I produce — Discovered by Cavendish in 1766.

Occurrence.—Occurs free in volcanic gases, in fire-damp, occluded in meteorites, in the gases exhaled from the lungs, and in those of the stomach and intestine. In combination in water, hydrogen sulfid, ammoniacal compounds, and in many organic substances.

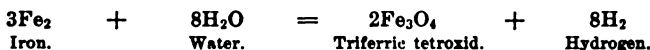
Preparation.—(1) By electrolysis of water, H is given off at the negative pole. Utilized when pure H is required.

(2) By the dissociation of water at very high temperatures.

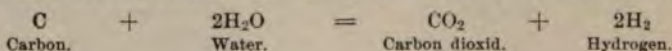
(3) By the decomposition of water by certain metals. The alkali metals decompose water at the ordinary temperature:



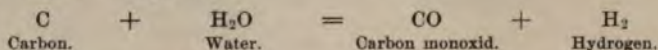
Some other metals, such as iron and copper, effect the decomposition only at high temperatures:



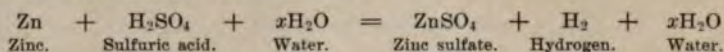
(4) By decomposition of water, passed over red-hot coke:



or at a higher temperature:



(5) By decomposition of mineral acids, in the presence of water, by zinc and certain other metals:



The water serves to dissolve the zinc sulfate. Chemically pure zinc, or zinc whose surface has been covered with an alloy of zinc and mercury, does not decompose the acid unless it forms part of a galvanic battery whose circuit is closed. The zincs of galvanic batteries are therefore covered with the alloy mentioned—are amalgamated—to prevent waste of zinc and acid.

This is the method usually resorted to for obtaining H. The gas so obtained, is, however, contaminated with small quantities of other gases, hydrogen phosphid, sulfid and arsenid.

Hydrogen, carbon dioxide, hydrogen sulfid, and other gases produced by the action of a liquid upon a solid at ordinary temperatures, are best prepared in one of the forms of apparatus shown in Figs. 25, 26 and 27.

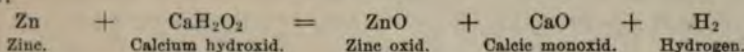
The solid material is placed in the larger bottle



Fig. 25.

(Fig. 25), or, over a layer of broken glass about five centimeters thick, in the bottle *a* (Fig. 26). The liquid reagent is from time to time introduced by the funnel tube, Fig. 25; or the bottle *b*, Fig. 26, is filled with it. The wash-bottles are partially filled with water to arrest any liquid or solid impurity. The apparatus, Figs. 26 and 27, have the advantage of being always ready for use. When the stopcock is open the gas escapes. When it is closed the internal pressure depresses the level of the liquid in *a* into the layer of broken glass, and the action is arrested. Kipp's apparatus, Fig. 27, is another convenient form of constant apparatus. The solid reagent is placed in the central bulb.

(6) By heating together a mixture of zinc dust and dry-slacked lime:



Properties.—*Physical.*—Hydrogen is a colorless, odorless, tasteless gas; 14.47 times lighter than air, being the lightest substance known. The weight of a litre, 0.0896 gram, is called a crith ($\kappa\rho\iota\theta\acute{\eta}$ = barleycorn). From this the weight of a litre of any gas may be calculated by multiplying half its molecular weight by .0896. It is almost insoluble in water and alcohol. It conducts heat and electricity better than any other gas. In obedience to the law: The diffusi-



FIG. 26.

bility of two gases varies inversely as the square roots of their densities, it is the most rapidly diffusible of gases. The rapidity with which this diffusion takes place renders the use of hydrogen, which has been kept for even a short time in gas-bags or gasometers, dangerous. It is liquefied at -240° (-400° F.) under a pressure of 13.3 atm. The liquid is clear and colorless, boils at -253° , only 20° above the absolute zero, and has a sp. gr. of 0.068.

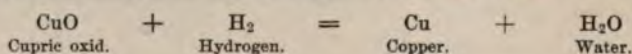


FIG. 27.

Certain metals have the power of absorbing large quantities of hydrogen, which is then said to be occluded. Palladium absorbs 980 volumes of the gas when used as the negative electrode in the electrolysis of water. The occluded gas is driven off by the application of heat, and possesses great chemical activity, similar to that which it has when in the nascent state. This latter quality, and the fact that heat is liberated during the occlusion, would seem to indicate that the gas is contained in the metal, not in a mere physical state of condensation, but in chemical combination.

Chemical.—Hydrogen exhibits no great tendency to combine with other elements at ordinary temperatures. It combines explosively,

however, with chlorin under the influence of sunlight, and with fluorin even in the dark. It does not support combustion, but, when ignited, burns with a pale blue and very hot flame; the result of the combination being water. Mixtures of hydrogen and oxygen explode violently on the approach of flame, or by the passage of the electric spark, the explosion being caused by the sudden expansion of the vapor of water formed, under the influence of the heat of the reaction. In a mixture of hydrogen and oxygen at the ordinary temperature formation of water takes place with extreme slowness (p. 91). If a piece of platinum foil be introduced into the mixture combination occurs with sensible rapidity, and, if the platinum be finely divided, the rapidity of the combination is such that the metal becomes incandescent, and explodes the mixture. The platinum here is said to be a **catalyser**, i.e., a substance by whose presence the velocity of a reaction is accelerated. Catalysers are also called **contact agents**. Many compounds containing oxygen give up that element when heated in an atmosphere of hydrogen:



The removal of oxygen from a compound is called a **reduction** or **deoxidation**. In a broader sense the term reduction is applied to any diminution in the relative quantity of the electro-negative factor in a compound. Thus mercuric chlorid, HgCl_2 (Hg 200: Cl 71) is *reduced* to mercurous chlorid, Hg_2Cl_2 (Hg 200: Cl 35.5).

At the instant that H is liberated from its compounds it has a deoxidizing power similar to that which ordinary H possesses only at elevated temperatures, and its tendency to combine with other elements is greater than under other conditions. The greater energy of H, and of other elements as well, in this **nascent state**, may be thus explained. Free H exists in the form of molecules, each one of which is composed of two atoms, but at the instant of its liberation from a compound, it is in the form of individual atoms, and that portion of force required to split up the molecule into atoms, necessary when free H enters into reaction, is not required when the gas is in the nascent state.

In its physical and chemical properties, this element more closely resembles those usually ranked as metals than it does those forming the class of non-metals, among which it is usually placed. Its conducting power, as well as its relation to the acids, which may be considered as salts of H, tend to separate it from the non-metals.

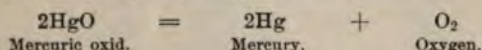
Analytical Characters.—(1) Burns with a faintly blue flame, which deposits water on a cold surface brought over it; (2) Mixed with oxygen, explodes on contact with flame, producing water.

OXYGEN.

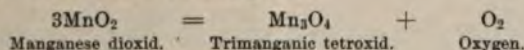
Symbol = O — *Bivalent* — *Atomic weight* = 15.87 (16); *molecular weight* = 31.74 (32) — *Sp. gr.* = 1.10563 A (*calculated* = 1.1088); 15.95 H; *sp. gr. of liquid* = 0.9787 — *One litre weighs 1.429 grams*; 100 *cubic inches weigh 34.27 grains* — *Name derived from* ὄξυς = *acid*, and γέννω = *I produce* — *Discovered by Mayow in 1674; rediscovered by Priestley in 1774.*

Occurrence.—Oxygen is the most abundant of the elements. It exists free in atmospheric air; in combination in a great number of substances, mineral, vegetable, and animal.

Preparation.—(1) By heating certain oxids:



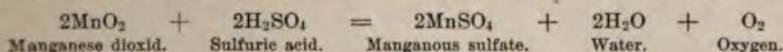
This was the method used by Priestley. 100 grams of mercuric oxid produce 5.16 litres of oxygen:



The black oxid of manganese is heated to redness in an iron or clay retort (Scheele, 1775); and 100 grams yield 8.51 litres of oxygen.

(2) By the electrolysis of water, acidulated with sulfuric acid, O is given off at the positive pole.

(3) By the action of sulfuric acid upon certain compounds rich in O: manganese dioxid, potassium dichromate, and plumbic peroxid:

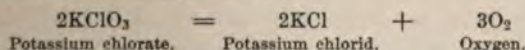


100 grams of manganese dioxid produce 12.83 litres of O.

(4.) By decomposing H_2SO_4 at a red heat, $2\text{H}_2\text{SO}_4 = 2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2$.

(5) By the decomposition by heat of certain salts rich in O: alkaline permanganates, nitrates, and chlorates.

The best method, and that usually adopted, is by heating a mixture of potassium chlorate and manganese dioxid in equal parts, moderately at first and more strongly toward the end of the reaction. The chlorate gives up all its O (27.33 litres from 100 grams of the salt), according to the equation:



At the end of the operation the manganese dioxid remains, apparently unchanged.

A small quantity of free chlorin usually exists in the gas pro-

duced by this reaction. If the oxygen is to be used for inhalation, the chlorine should be removed by allowing the gas to stand over water for 24 hours.

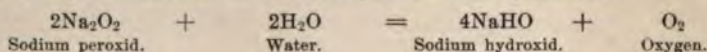
When heat is required for the generation of gases the operation is conducted in retorts of glass or metal, or in the apparatus shown in Fig. 28. If the gas be collected over water the disengagement tube



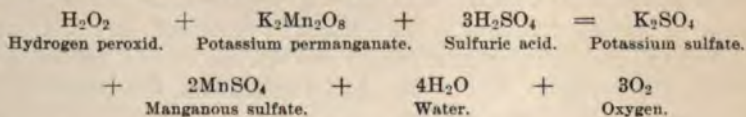
FIG. 28.

must be withdrawn from the water, before the source or heat is removed. Neglect of this precaution will cause an explosion, by the entrance of water into the hot flask, by the contraction of the gas contained in it, on partial cooling.

(6) By the action of water upon sodium peroxid :



(7) By the mutual decomposition of potassium permanganate and hydrogen peroxid, in the presence of sulfuric acid:



One kilo H_2O_2 (3 per cent) and 500 cc. dilute H_2SO_4 (1:5) are placed in the generating flask and 56 grams $\text{K}_2\text{Mn}_2\text{O}_8$, dissolved in H_2O , are gradually added. With these quantities 20 litres O are obtained.

(8) By the action of dilute hydrochloric acid upon a mixture of 2

parts barium peroxid, 1 part manganese dioxid, and 1 part plaster of Paris, compressed into cubes about $1\frac{1}{2}$ cent. square.

Methods 6, 7, and 8 have the advantage that heat is not required, and the forms of apparatus, Figs. 25, 26 and 27, may be used.

Properties.—*Physical.*—Oxygen is a colorless, odorless, tasteless gas, soluble in water in the proportion of 7.08 cc. in 1 litre of water at 14.8° (58.6° F.), somewhat more soluble in absolute alcohol. It liquefies at -140° (-220° F.) under a pressure of 300 atmospheres. Liquid oxygen boils at -187.4° (-294.5° F.) at the ordinary pressure. The sp. gr. of liquid oxygen is 0.9787.

Chemical.—Oxygen is characterized, chemically, by the strong tendency which it exhibits to enter into combination with other elements. It forms binary compounds with all elements except fluorin and bromin. With most elements it unites directly, especially at elevated temperatures. In many instances this union is attended by the appearance of light, and always by the extrication of heat. The luminous union of O with another element constitutes the familiar phenomenon of **combustion**, and is the principal source from which we obtain so-called artificial heat and light. A body is said to be **combustible** when it is capable of so energetically combining with the oxygen of the air as to liberate light as well as heat. Gases are said to be **supporters of combustion**, when combustible substances will unite with them, or with some of their constituents, the union being attended with the appearance of heat and light. The distinction between combustible substances and supporters of combustion is, however, one of mere convenience. The action taking place between the two substances, one is as much a party to it as the other. A jet of air burns in an atmosphere of coal-gas as readily as a jet of coal-gas burns in air.

An oxidation is a chemical action in which oxygen combines with an element or a compound. The burning of coal: $C + O = CO$ or $C + O_2 = CO_2$; and the formation of acetic acid from alcohol: $C_2H_5O + O_2 = C_2H_4O_2 + H_2O$, are oxidations. In a broader sense the word "oxidation" is sometimes used as the opposite to "reduction" (p. 62) to apply to any increase in the relative quantity of the electro-negative element in a compound. Thus the conversion of $FeCl_2$ (Fe 112:Cl 142) into Fe_2Cl_6 (Fe 112:Cl 213) may be referred to as an oxidation, although it is, more properly, a chlorination.

The compounds of oxygen—the **oxids**—are divisible into three groups:

1. **Anhydrids.**—Oxids capable of combining with water to form *acids*. Thus *sulfuric anhydrid*, SO_3 , unites with water to form *sulfuric acid*, H_2SO_4 .

The term anhydrid is not limited in application to *binary com-*

pounds, but applies to any substance capable of combining with water to form an acid. Thus the compound $C_4H_6O_3$ is known as acetic anhydrid, because it combines with water to form acetic acid: $C_4H_6O_3 + H_2O = 2C_2H_4O_2$. (See compounds of arsenic and sulfur.)

2. **Basic oxids** are such as combine with water to form bases. Thus calcium oxid, CaO , unites with water to form calcium hydroxid, CaH_2O_2 .

3. **Saline, neutral or indifferent oxids** are such as are neither acid nor basic in character. In some instances they are essentially neutral, as in the case of the protoxid of hydrogen, or water. In other cases they are formed by the union of two other oxids, one basic, the other acid in quality, such as the red oxid of lead, Pb_3O_4 , formed by the union of a molecule of the acidulous peroxid, PbO_2 , with two of the basic protoxid, PbO . It is to oxids of this character that the term "saline" properly applies.

The process of respiration is very similar to combustion, and as oxygen gas is the best supporter of combustion, so, in the diluted form in which it exists in atmospheric air, it is not only the best, but the only supporter of animal respiration. (See Carbon dioxid.)

Analytical Characters.—1. A glowing match-stick bursts into flame in free oxygen. 2. Free O, when mixed with nitrogen dioxid, produces a brown gas.

Ozone.—*Allotropic oxygen.*—Air through which discharges of static electricity have been passed, and oxygen obtained by the decomposition of water (if electrodes of gold or platinum be used), have a peculiar odor, somewhat resembling that of sulfur, which is due to the conversion of a part of the oxygen into ozone.

Ozone is produced: 1. By the decomposition of water by the battery. 2. By the slow oxidation of phosphorus in damp air. 3. By the action of concentrated sulfuric acid upon barium dioxid. 4. By the passage of silent electric discharges through air or oxygen.

In the preparation of ozonized oxygen the best results are obtained by passing a slow current of oxygen through an apparatus made entirely of glass and platinum, cooled by a current of cold water, and traversed by the invisible discharge of an induction coil.

Pure, liquid ozone has been obtained by subjecting ozonized oxygen to the temperature of liquid oxygen at the atmospheric pressure. It is a dark blue liquid, almost opaque in layers 2 mm. thick, which is not decomposed at the ordinary temperature, but converted into a bluish gas. It boils at -119° ($-182.2^\circ F.$).

When oxygen is ozonized it contracts slightly in volume, and when the ozone is removed from ozonized oxygen by mercury or potassium iodid the volume of the gas is not diminished. These facts, and the great chemical activity of ozone, have led chemists

to regard it as condensed oxygen; the molecule of ozone being represented thus (OOO), while that of ordinary oxygen is (OO).

Ozone is very sparingly soluble in water, more soluble in the presence of hypophosphites, insoluble in solutions of acids and alkalis. In the presence of moisture it is slowly converted into oxygen at 100° (212° F.), a change which takes place rapidly and completely at 237° (459° F.) It is a powerful oxidant; it decomposes solutions of potassium iodid with formation of potassium hydroxid, and liberation of iodine; it oxidizes all metals except gold and platinum, in the presence of moisture; it decolorizes indigo and other organic pigments, and acts rapidly upon rubber, cork, and other organic substances.

Analytical Characters.—1. Neutral litmus paper, impregnated with solution of potassium iodid, is turned blue when exposed to air containing ozone. The same litmus paper without iodid is not affected. 2. Manganous sulfate solution is turned brown by ozone. 3. Solutions of thalious salts are colored yellow or brown by ozone. 4. Paper impregnated with fresh tincture of natural (unpurified) guaiacum is colored blue by ozone. 5. Paper impregnated with solution of manganous sulfate, or lead hydroxid, or palladium chlorid is colored dark brown or black by ozone. 6. Metallic silver is blackened by ozone.

When inhaled, air containing 0.07 gram of ozone per litre causes intense coryza and hæmoptysis. It is probable that ozone is by no means as constant a constituent of the atmosphere as was formerly supposed. (See Hydrogen dioxid.)

COMPOUNDS OF HYDROGEN AND OXYGEN.

Two are known—hydrogen oxid or water, H_2O ; hydrogen peroxid or oxygenated water, H_2O_2 .

WATER.

H_2O —Molecular weight=18 Sp. gr.=1—Vapor density=0.6218 A; calculated=0.6234—Composition discovered by Priestley in 1780—1 cc. weighs 1 gm. at 4° and 0.999 gm. at 16° —1 cubic inch weighs 252.6 grains at 60° F.

Occurrence.—In unorganized nature H_2O exists in the gaseous form in atmospheric air and in volcanic gases; in the liquid form very abundantly; and as a solid in snow, ice, and hail.

As water of crystallization it exists in definite proportions in certain crystals, to the maintenance of whose shape it is necessary.

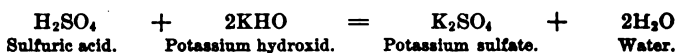
In the organized world H_2O forms a constituent part of every tissue and fluid.

Formation.—Water is formed: 1. By union, brought about by elevation of temperature, of one vol. O with two vols. H.

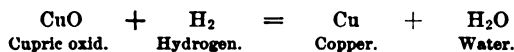
2. By burning H, or substances containing it, in air or in O.

3. By heating organic substances containing H to redness with cupric oxid, or with other substances capable of yielding O. This method of formation is utilized to determine the amount of H contained in organic substances.

4. When an acid and a hydroxid react upon each other to form a salt:



5. When a metallic oxid is reduced by hydrogen:



6. In the reduction and oxidation of many organic substances.

Pure H_2O is not found in nature. When required free from ordinary impurities it is separated from suspended matters by filtration, and from dissolved substances by distillation.

Properties.—*Physical.*—With a barometric pressure of 760 mm. H_2O is solid below 0° (32° F.); liquid between 0° (32° F.) and 100° (212° F.); and gaseous above 100° (212° F.). When H_2O is enclosed in capillary tubes, or is at complete rest, it may be cooled to -15° (5° F.) without solidifying. If, while at this temperature, it be agitated, it solidifies instantly, and the temperature suddenly rises to 0° (32° F.). The melting-point of ice is lowered 0.0075° (0.0135° F.) for each additional atmosphere of pressure.

The boiling-point is subject to greater variations than the freezing-point. It is the lower as the pressure is diminished, and the higher as it is increased. Advantage is taken of the reduced boiling-point of solutions in vacuo for the separation of substances, such as cane sugar, which are injured at the temperature of boiling H_2O . On the other hand, the increased temperature that may be imparted to liquid H_2O under pressure is utilized in many processes in the laboratory and in the arts, for effecting solutions and chemical actions which do not take place at lower temperatures. The boiling-point of H_2O holding solid matter in solution is higher than that of pure H_2O , the degree of increase depending upon the amount and nature of the substance dissolved. On the other hand, mixtures of H_2O with liquids of lower boiling-point boil at temperatures less than 100° (212° F.). Although the conversion of water into water-vapor takes place most actively at 100° (212° F.), water and ice evaporate at all temperatures.

Water is the best solvent we have, and acts in some instances as a simple solvent, in others as a chemical solvent.

Vapor of water is colorless, transparent, and invisible. Sp. gr. 0.6234 A or 9 H. A litre of vapor of water weighs 0.8064. The latent heat of vaporization of water is 536.5; that is, as much heat is required to vaporize 1 kilo. of water at 100° as would suffice to raise 536.5 kilos. of water 1° in temperature. In passing from the liquid to the gaseous state, water expands 1,696 times in volume.

Chemical.—Water may be shown to consist of 1 vol. O and 2 vols. H, or 8 by weight of O and 1 by weight of H, either by analysis or synthesis.

Analysis is the reducing of a compound to its constituent parts or elements.

Synthesis is the formation of a compound from its elements. A partial synthesis is one in which a complex compound is produced from a simpler one, but not from the elements.

Water may be resolved into its constituent gases: 1. By electrolysis of acidulated water; H being given off at the negative and O at the positive pole. 2. By passing vapor of H_2O through a platinum tube heated to whiteness, or through a porcelain tube heated to about $1,100^{\circ}$. The decomposition of a compound gas or vapor by elevation of temperature is called **dissociation**. 3. By the action of the alkali metals. Hydrogen is given off, and the metallic hydroxid remains in solution in an excess of H_2O . 4. By passing vapor of H_2O over red-hot iron. Oxid of iron remains and H is given off.

Water combines with oxids to form new compounds, some of which are acids and others bases, known as **hydroxids**.

A **hydroxid** is a compound formed by the replacement of half of the hydrogen of water by another element or by a radical.

A **hydrate** is a compound containing chemically combined water. The act of union of a substance with water is referred to as **hydration**.

The hydroxids of the electro-negative elements and radicals are **acids**; most of those of the electro-positive elements and radicals are **basic hydroxids**.

Certain substances, in crystallizing, combine with a definite proportion of water, which is known as **water of crystallization**, and whose presence, although necessary to the maintenance of certain physical characters, such as color and crystalline form, does not modify their chemical reactions. In many instances a portion of the water of crystallization may be driven off at a comparatively low temperature, while a higher temperature is required to expel the remainder. This latter is known as **water of constitution**.

The symbol Aq (Latin, *aqua*) is frequently used to designate the water of crystallization, the water of constitution being indicated by H_2O . Thus $MgSO_4 \cdot H_2O + 6Aq$ represents magnesium sulfate with one molecule of water of constitution and six molecules of water of crystallization. We consider it preferable, however, as the distinction between water of crystallization and water of constitution in many salts is only one of degree and not of kind, to use the symbol Aq to designate the sum of the two; thus, $MgSO_4 + 7Aq$.

Water decomposes the chlorids of the second class of elements (those of carbon only at high temperatures and under pressure). Thus phosphorous trichlorid forms phosphorous and hydrochloric acids: $PCl_3 + 3H_2O = H_3PO_3 + 3HCl$. A decomposition attended with absorption of water is called **hydrolysis**.

Natural Waters.—Natural waters which appear to the senses to be fit for drinking are called **potable waters**, in contradistinction to such as are, from their taste and appearance, obviously unfit for that use.

Potable waters may be classified, according to their origin, into four groups:

Meteoric waters: rain water and melted snow. These are the purest natural waters if uncontaminated; they contain very small quantities of solids, and are highly aerated. Rain water falling during the first part of a shower is less pure than that which falls subsequently. In districts where notable quantities of coal which contains sulfur are burnt, rain water contains more sulfates, ammoniacal salts, nitrates and nitrites than elsewhere.

Surface waters: the waters of rivers, lakes and ponds. These are mixtures, in varying proportions, of rain water, spring water and the drainage of the surrounding land. They vary greatly in natural purity, and are frequently contaminated by sewage and other refuse.

Ground waters: water which permeates the superficial stratum above the uppermost impermeable rock. This is the water obtained in surface wells and in driven wells. Its quality depends upon what is in and on the stratum in which the well is dug; a driven well in a sandy stratum remote from habitations yields an excellent water, while the water of a well near a privy vault or a defective sewer is more or less diluted sewage. In limestone districts ground water is hard.

Deep waters: spring waters and those of artesian wells.

Spring water is rain water which, having percolated through a portion of the earth's crust (in which it may also have been subjected to pressure), has become charged with solid and gaseous matter, varying in kind and quantity according to the nature of the strata

through which it has percolated, the duration of contact, and the pressure to which it was subject during such contact.

Spring waters from igneous rocks and from the older sedimentary formations are fresh and sweet, and any spring water may be considered such whose temperature is less than 20° (68° F.), and which does not contain more than 40 parts in 100,000 of solid matter; provided that a large proportion of the solid matter does not consist of salts having a medicinal action, and that sulfurous gases and sulfids are absent.

Artesian wells are artificial springs, produced by boring in a low-lying district, until a pervious layer, between two impervious strata, is reached; the outcrop of the system being in an adjacent elevated region.

Impurities in Potable Waters.—A water to be fit for drinking purposes should be cool, limpid and odorless; it should have an agreeable taste, neither flat, salty, nor sweetish, and it should dissolve soap readily, without formation of any flocculent precipitate. But, while it is safe to condemn a water which does not possess the above characters, it is by no means safe to regard all waters which do possess them as beyond suspicion. The most dangerous of all contaminations of drinking waters is by admixture of sewage, which may be present in a water in quantity sufficient to render it unfit for use and the water yet retain all of the characters of a good water above referred to. To determine whether a water is really fit for drinking a chemical analysis is necessary, and a bacteriological examination is desirable. For the methods of chemical analysis the student is referred to treatises on that subject. The constituents usually determined, and the interpretation of the results, are as follows:

Total Solids.—The amount of solid material dissolved in potable waters varies from 4.3 to 50 in 100,000 (2.5 to 29.2 grains per U. S. gal.); and a water containing more than the latter quantity is to be condemned on that account alone.

Chlorids.—The presence of the chlorids of the alkaline metals, in quantities not sufficient to be detectable by the taste, is of no importance *per se*; but in connection with the presence of organic impurity, a determination of the amount of chlorin affords a ready method of indicating the probable source of the organic contamination. As vegetable organic matter brings with it but small quantities of chlorids, while animal contaminations are rich in those compounds, the presence of a large amount of chlorin serves to indicate that organic impurity is of animal origin. Indeed, when time presses, as during an epidemic, it is best to rely upon determinations of chlorin, and condemn all waters containing more than 1.7 in 100,000 (1 grain per U. S. gal.) of that element.

Hardness.—The greater part of the solid matter dissolved in natural fresh waters consists of the salts of calcium, accompanied by less quantities of the salts of magnesium. The calcium salt is usually the bicarbonate or the sulfate; sometimes the chlorid, phosphate, or nitrate.

A water containing an excess of calcareous salt is said to be **hard**, and one not so charged is said to be **soft**. If the hardness be due to the presence of the bicarbonate it is **temporary**, if due to the sulfate it is **permanent**. Calcium carbonate is almost insoluble in pure water, but in the presence of free carbonic acid the more soluble bicarbonate is dissolved. But, on the water being boiled, it is decomposed, with precipitation of the carbonate. As calcium sulfate is held in solution by virtue of its own, albeit sparing, solubility, it is not deposited when the water is boiled.

The hardness is now usually reported in terms of calcium carbonate, CaCO_3 , either in grains per gallon or parts in 100,000. It is also sometimes reported in "degrees," which represent grains of CaCO_3 per imperial gallon. Very soft waters contain about 5CaCO_3 in 100,000, and hard waters 15 or over. Usually a water containing more than 20CaCO_3 in 100,000 is considered too hard for domestic use, unless softened by boiling. But a water is not to be condemned solely because its hardness exceeds this limit, because in certain limestone districts all waters are very hard.

Waters which owe their hardness to excess of magnesium salts, cause intestinal disturbances in those not habituated to them.

Organic Matter.—Technically, organic impurities in a water consist of vegetable or animal matters containing nitrogen. We have seen that the quantity of chlorin affords an indication as to whether the organic impurity found to be present is of vegetable or of animal origin. Animal organic contamination has its origin in sewage, and its presence consequently indicates that the water is, or may at any moment become, the means of transmitting water-borne diseases, such as typhoid and cholera.

The nitrogenous substances in feces and urine consist of albuminous bodies, crystalline organic compounds (such as urea, leucin, etc.) and ammoniacal salts. By the action of micro-organisms, which exist in the soil and in water, the albuminous and crystalline compounds are gradually converted into ammonium compounds, which are subsequently oxidized by atmospheric or dissolved oxygen, aided by bacterial influence, to nitrites and later to nitrates. Consequently the amount of sewage contamination, and the degree in which such contamination has been subsequently modified, can be inferred from quantitative determinations of the nitrogen present in the several forms referred to.

In the usual process of water analysis the following factors are determined quantitatively:

A. Albuminoid ammonia, which represents the nitrogen present in albuminous and crystalline combination.

B. Free ammonia, which represents the ammoniacal compounds.

C. Nitrogen in nitrates and nitrites, and D. Nitrites.

If a water yield no albuminoid ammonia it is organically pure, even if it contain much free ammonia and chlorids. If it contain from .02 to .05 milligrams per litre (.002 to .005 in 100,000) it is still quite pure. When the albuminoid ammonia reaches 0.1 milligr. per litre (.01 in 100,000) the water is to be looked upon with suspicion; and it is to be condemned when the proportion reaches 0.15 (.015 in 100,000). When free ammonia is also present in considerable quantity, a water yielding 0.05 (.005 in 100,000) of albuminoid ammonia is to be looked upon with suspicion.

Nitrates and nitrites are present in rain water in quantities less than 0.5 parts in 100,000, calculated as nitrogen. When the amount exceeds this, these salts are considered as indicating previous contamination by organic matter which has been oxidized and whose nitrogen has been to some extent converted into nitrites and nitrates.

The quantity of nitrites in good waters does not exceed .002 in 100,000 when they are present. A larger quantity is considered as indicating previous organic contamination.

In some processes it is sought to measure the organic contamination by the amount of oxygen consumed in their oxidation by potassium permanganate. As these results take no account of other oxidations which may take place they are not reliable.

Poisonous Metals.—Natural waters containing notable quantities of iron compounds belong to the class of chalybeate mineral waters. Contact with metallic iron does not contaminate water. In districts where copper deposits exist the waters sometimes contain copper, and the waters of some streams contain arsenic.

Lead in drinking water has been a prolific source of chronic lead poisoning. As lead is only dissolved by water after oxidation, conditions favoring oxidation of the metal favor its solution. Such conditions are: the presence of nitrates, a highly aerated condition of the water, alternate wetting and drying of the surface of the metal, the absence of sulfates and carbonates, and the presence of much carbonic acid dissolved under pressure (soda water). Sulfates and carbonates prevent solution by the formation of a protecting coating of an insoluble salt. As a rule, the purer the water the more liable it is to dissolve lead when brought in contact with that metal, especially if the contact occur when the water is at a high temperature, or when it lasts for a long period.

Bacteriological Examination of Water.—In recent years much attention has been given to the examination of natural waters by bacteriological methods, plate cultures on gelatin, cultures in blood serum and on potatoes, and experiments on animals. Although in some instances pathogenic bacteria have been found in water, and although in the future valuable results will probably be obtained by these methods, the chief reliance in determining the quality of a drinking-water is still to be placed upon the older chemical processes.

Purification of Water.—The artificial means of rendering a more or less contaminated water fit for use are of five kinds: Distillation, subsidence, filtration, precipitation, and boiling.

Distillation is resorted to in the laboratory to obtain very pure water, also, on a larger scale, to purify drinking water. When distilled water is to be used for drinking it should be aerated and charged with salts to the extent of about 0.03 gram each of calcium bicarbonate and sodium chlorid to the litre.

In filtration suspended impurities are removed more or less completely by passing the water through a porous material. In *filter beds*, used to filter large quantities of water, sand is the filtering material used, either alone or combined with charcoal or spongy iron. In domestic filters, treating small quantities of water, the filtering material is quartz sand, charcoal, porous stone, or unglazed earthenware or porcelain. Whatever may be the size or construction of the filter, it must be cleaned periodically. If this be neglected the filter ceases to purify the water, and becomes itself a source of contamination. The usual method of cleaning is by reversing the current through the filter until the washings come away clear. Dissolved organic matter is in part removed by oxidation in filtration through sand filter beds several feet in thickness, or through much thinner layers of charcoal or porous iron. Typhoid and cholera germs pass, although in greatly diminished numbers, through all filters except those made of unglazed porcelain.

Precipitation methods were formerly used only to soften temporarily hard waters. One method consists in the addition of lime water in quantity just sufficient to convert the soluble calcium bicarbonate present into the insoluble carbonate. At present precipitation methods are also used, in combination with subsidence and filtration, to remove organic impurities; alum or a ferric salt is added, an excess being avoided, to form a gelatinous precipitate which carries the impurities down with it mechanically as it settles when the water is left at rest in the subsidence tanks; the water is drawn off from above the deposit to the filters, after a proper interval. Precipitation and subsidence are thus used to diminish the work required of the filters.

The purification of water by boiling can only be carried on on a small scale. It is very useful, however, to soften temporarily hard waters and, particularly, to sterilize infected waters. For the latter purpose the boiling must be continued actively for at least twenty minutes in a vessel closed except for a steam outlet, which is to be stopped with a plug of cotton when the vessel is taken off to cool.

Natural Purification of Water.—The water of brooks, rivers, and lakes which have been contaminated by sewage and other organic impurity becomes gradually purified by natural processes. Suspended particles are deposited upon the bottom and sides of the stream, more or less rapidly, according to their gravity and the rapidity of the current. The bicarbonates of calcium, magnesium, and iron gradually lose carbon dioxid, and are precipitated as carbonates, which mechanically carry down dissolved as well as suspended impurities. The decompositions, oxidations, and reductions to which organic matters are subject under the influence of atmospheric and dissolved oxygen and bacterial action bring about their gradual mineralization by conversion into ammonia and then into nitrates. The processes of nutrition of aquatic plant life absorb dissolved organic impurity, as well as the products of decomposition of nitrogenized substances. This natural purification proceeds the more rapidly the more contact with air is favored.

Mineral Waters.—Under this head are classed all waters which are of therapeutic or industrial value, by reason of the quantity or nature of the dissolved solids which they contain; or which have a temperature greater than 20° (68° F.).

The composition of mineral waters varies greatly, according to the nature of the strata or veins through which the water passes, and to the conditions of pressure and previous composition under which it is in contact with these deposits.

Although a sharply defined classification of mineral waters is not possible, one which is useful, if not accurate, may be made, based upon the predominance of some constituent, or constituents, which impart to the water a well-defined therapeutic value. A classification which has been generally adopted includes five classes:

I. *Acidulous waters*; whose value depends upon dissolved carbonic acid. They contain but small quantities of solids, principally the bicarbonates of sodium and calcium and sodium chlorid.

II. *Alkaline waters*; which contain quantities of the bicarbonates of sodium, potassium, lithium, and calcium, sufficient to communicate to them an alkaline reaction, and frequently a soapy taste; either naturally, or after expulsion of carbon dioxid by boiling.

III. *Chalybeate waters*; which contain salts of iron in greater proportion than 4 parts in 100,000. They contain ferrous bicar-

bonate, sulfate, crenate, and apocrenate, calcium carbonate, sulfates of potassium, sodium, calcium, magnesium, and aluminium, notable quantities of sodium chlorid, and frequently small amounts of arsenic. They have the taste of iron and are usually clear as they emerge from the earth. Those containing ferrous bicarbonate deposit a sediment on standing, by loss of carbon dioxid, and formation of ferrous carbonate.

IV. *Saline waters*; which contain neutral salts in considerable quantity. The nature of the salts which they contain is so diverse that the group may well be subdivided:

a. *Chlorin waters*; which contain large quantities of sodium chlorid, accompanied by less amounts of the chlorids of potassium, calcium, and magnesium. Some are so rich in sodium chlorid that they are not of service as therapeutic agents, but are evaporated to yield a more or less pure salt. Any natural water containing more than 300 parts in 100,000 of sodium chlorid belongs to this class, provided it do not contain substances more active in their medicinal action in such proportion as to warrant its classification elsewhere. Waters containing more than 1,500 parts in 100,000 are too concentrated for internal administration.

β. *Sulfate waters* are actively purgative from the presence of considerable proportions of the sulfates of sodium, calcium, and magnesium. Some contain large quantities of sodium sulfate, with mere traces of the calcium and magnesium salts, while in others the proportion of the sulfates of magnesium and calcium is as high as 3,000 parts in 100,000 to 2,000 parts in 100,000 of sodium sulfate. They vary much in concentration; from 500 to nearly 6,000 parts of total solids in 100,000. They have a salty, bitter taste, and vary much in temperature.

γ. *Bromin and iodin waters* are such as contain the bromids or iodids of potassium, sodium, or magnesium in sufficient quantity to communicate to them the medicinal properties of those salts.

V. *Sulfurous waters*; which hold hydrogen sulfid or metallic sulfids in solution. They have a disagreeable odor and are usually warm. They contain 20 to 400 parts in 100,000 of total solids.

Physiological.—Water is taken into the body both as a liquid and as a constituent of every article of food; the amount ingested by a healthy adult being 2.25 to 2.75 litres ($2\frac{1}{8}$ to 3 quarts) per diem. The greater the elimination and the drier the nature of the food the greater is the amount of H_2O taken in the liquid form.

Water is a constituent of every tissue and fluid of the body, varying from 0.2 per cent. in the enamel of the teeth to 99.5 per cent. in the perspiration and saliva. It constitutes about 60 per cent. of the weight of the body.

The consistency of the various parts does not depend entirely upon the relative proportion of solids and H_2O , but is influenced by the nature of the solids. The blood, although liquid in the ordinary sense of the term, contains a less proportional amount of H_2O than does the tissue of the kidneys, and about the same proportion as the tissue of the heart. Although the bile and mucus are not as fluid as the blood, they contain a larger proportion of H_2O to solids than does that liquid.

Water is discharged by the kidneys, intestines, skin, and pulmonary surfaces. The quantity discharged is greater than that ingested; the excess being formed in the body by the oxidation of the H of its organic constituents.

HYDROGEN DIOXID.

HYDROGEN PEROXID—OXYGENATED WATER.

H_2O_2 —*Molecular weight* = 34—*Sp. gr.* = 1.455—*Discovered by Thénard in 1818.*

Exists naturally in very minute quantity in rain-water, in air, and in the saliva.

This substance may be obtained in a state of purity by accurately following the process of Thénard. It may also be obtained, mixed with a large quantity of H_2O , by the action of dilute mineral acids on barium peroxid: $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$. It is also formed in small quantity during the slow oxidation of many elements and compounds, such as P, Pb, Zn, Cd, Al, alcohol, ether and the essences.

It is prepared industrially of 10–12 volume strength by gradually adding barium peroxid to dilute hydrofluoric acid solution, the mixture being maintained at a low temperature and constantly agitated; or, in still greater concentration by the action of dilute acids on sodium peroxid, care being had to prevent heating of the mixture: $Na_2O_2 + 2HCl = 2NaCl + H_2O_2$. Hydrogen peroxid is also formed when sodium peroxid is dissolved in water: $Na_2O_2 + 2H_2O = 2NaHO + H_2O_2$.

The pure substance is a colorless, syrupy liquid, which, when poured into H_2O , sinks under it before mixing. It has a disagreeable metallic taste, somewhat resembling that of tartar emetic. When taken into the mouth it produces a tingling sensation, increases the flow of saliva, and bleaches the tissues with which it comes in contact. It is still liquid at -30° (-22° F.). It is very unstable, and, even in darkness and at ordinary temperature, is gradually decomposed. At 20° (68° F.) the decomposition takes place more quickly and at 100° (212° F.) rapidly and with effervescence. The dilute substance, however, is comparatively stable, and may be boiled and even distilled without suffering decomposition. Yet it is liable to

explosive decomposition when exposed to summer temperature in closed vessels.

Hydrogen peroxid acts both as a reducing and an oxidizing agent. Arsenic, sulfids, and sulfur dioxid are oxidized by it at the expense of half its oxygen. When it is brought in contact with silver oxid both substances are violently decomposed, water and elementary silver remaining. By certain substances, such as gold, platinum, and charcoal in a state of fine division, fibrin, or manganese dioxid, it is decomposed with evolution of oxygen; the decomposing agent remaining unchanged.

The pure substance, when decomposed, yields 475 times its volume of oxygen; the dilute 15 to 20 volumes.

In dilute solution it is used as a bleaching agent and in the renovation of old oil-paintings. It is an energetic disinfectant and antiseptic, and is extensively used in surgery. "Ozonic ether" is a mixture of ethylic ether and dilute hydrogen peroxid.

Analytical Characters.—1. To a solution of starch a few drops of cadmium iodid solution are added, then a small quantity of the fluid to be tested, and, finally, a drop of a solution of ferrous sulfate. A blue color is produced in the presence of hydrogen peroxid, even if the solution contain only 0.05 milligram per litre.

2. Add freshly-prepared tincture of guaiacum and a few drops of a cold infusion of malt. A blue color—1 in 2,000,000.

3. Add to the liquid a few drops of potassium dichromate and a little dilute sulfuric acid, and agitate with ether. The ether assumes a brilliant blue-violet color.

4. Add to 6 cc. of the liquid sulfuric acid, iodid of zinc, starch-paste, two drops of a 2 per cent. solution of cupric sulfate, and a little one-half per cent. solution of ferrous sulfate, in the order named. A blue color.

5. Add a trace of acetic acid, some α naphthylamin and solid sodium chlorid. After a short time a blue or blue-violet color, and after some hours a flocculent ppt. of the same color.

Atmospheric Hydrogen Dioxid.—It has been claimed that atmospheric air, rain-water, snow, and hoar-frost constantly contain small quantities of hydrogen peroxid; the amount in rain-water varying from 0.0008 to 0.05 part in 100,000. The most recent experiments bearing upon the supposed presence of ozone and hydrogen peroxid in atmospheric air seem, however, to justify the belief that those substances, if present in air at all, are not met with in the amounts and with the constancy that have been claimed. According to this latter view the appearances from which the presence of ozone and hydrogen peroxid has been inferred are not caused by those substances, but by nitrous acid and the oxids of nitrogen.

CLASS II—ELEMENTS WHICH FORM NO COMPOUNDS.

HELIUM. NEON. ARGON. KRYPTON. XENON.

The elements of this group have been recently discovered, and exist in air and in certain minerals. As they form no compounds, their atomic weights are not known, although, from their molecular heats, there is reason to believe that their molecular symbols are He, etc., not He_2 , etc.

Argon, the most abundant of the class, was discovered by Rayleigh and Ramsay in 1894 in air, in which it exists in the proportion of 0.9 in 100 by volume, and 1.2 per cent by weight. It is a transparent, colorless, odorless, tasteless gas; sp. gr.=19.941; Mw.=39.9. At the normal pressure it liquefies, at -186.9° , forming a colorless liquid of sp. gr. 1.5. It solidifies at -190° . It is sparingly soluble in water: 4.05 in 100. It is obtained from atmospheric air as a residue by causing the other constituents to enter into combination. When rarified it gives a characteristic spectrum of many lines with the induction spark.

Helium owes its name to the fact that its existence in the sun's atmosphere was recognized by the characteristic line D_α of the solar spectrum before it was discovered as a terrestrial element. It exists in certain rare uranium minerals, and in some spring waters. It is a very light gas: Mw.=4.

The other members of the class: **Neon**: Mw.=20; **Krypton**: Mw.=81.8; and **Xenon**: Mw.=128, have been found in small amount in the residue of evaporation of liquefied air.

CLASS III—ACIDULOUS ELEMENTS.

Elements all of whose Hydrates are Acids, and which do not form Salts with the Oxacids.

I. CHLORIN GROUP.

FLUORIN. CHLORIN. BROMIN. IODIN.

The elements of this group, known as the **halogens**, closely resemble each other in their chemical properties and in the structure and properties of their compounds, fluorin differing more from the other three than these do from each other. They are univalent in the great majority of the compounds into whose formation they enter, although they are sometimes trivalent, as in ICl_3 . With hydrogen each forms an acid compound, composed of one volume of the halogen in the gaseous state with one volume of hydrogen. All mineral acids into whose composition they enter are monobasic. Fluorin is a

gas, liquefiable with difficulty, chlorin an easily liquefiable gas, bromin a liquid, and iodin a solid at the ordinary temperature and pressure. The relations of their compounds to each other are shown in the following table:

HF	—	—	—	—	—	—
HCl	Cl ₂ O	Cl ₂ O ₄	HCIO	HClO ₂	HClO ₃	HClO ₄
HBr	—	—	HBrO	—	HBrO ₃	HBrO ₄
HI	—	I ₂ O ₄	HIO	HIO ₂	HIO ₃	HIO ₄
Hydro-ic acid.	Monoxid.	Tetroxid.	Hypo- ous acid.	-ous acid.	-ic acid.	Per-ic acid.

The heats of formation of the halogen hydracids diminish from fluorin to iodin: HF=+38,495 cal; HCl=+21,997 cal; HBr=+8,368 cal; and HI=-7,217 cal, and the elements displace each other from their binary compounds in the same order, i. e., the fluorin compounds are the most stable and those of iodin the least so. In the oxygen compounds the conditions are reversed. Fluorin forms no oxygen compound, and of the other three the order of stability is: iodin, chlorin, bromin. The heats of formation of the -ic acids are: HIO₃=+55,950 cal; HClO₃=+23,910; and HBrO₃=+12,194 cal. The heats of neutralization of hydrochloric, hydrobromic and hydriodic acids are normal: 13,700 cal; that of hydrofluoric acid is abnormal: 16,270 cal. Therefore, hydrofluoric acid is a weaker acid than the others, being less perfectly dissociated (p. 100).

FLUORIN

Symbol=F—*Atomic weight*=19 (O=16: 19; H=1: 18.85)—*Sp. gr.* 1.265 A (*calculated*=1.316)—*Discovered by* Sir H. Davy in 1812.

Fluorin has been isolated by the electrolysis of pure, dry HF at—23° (—9.4° F.). It exists in nature chiefly in *Fluor Spar*, CaF₂, and in *cryolite*, Al₂F₆ (NaF)₆.

It is a gas, colorless in thin layers, greenish yellow in thick layers. It decomposes H₂O, with formation of HF and ozone. In it Si, B, As, Sb, S, and I fire spontaneously. With H it detonates, even in the dark. It attacks organic substances violently. The apparatus in which it is liberated must be made of platinum or fluor-spar. It forms compounds with all other elements except oxygen.

Hydrogen Fluorid.—*Hydrofluoric acid*=HF—*Molecular weight*=20. Hydrofluoric acid is obtained by the action of an excess of sulfuric acid upon fluor-spar or upon barium fluorid, with the aid of gentle heat: CaF₂+H₂SO₄=CaSO₄+2HF. If a solution be desired, the operation is conducted in a platinum or lead retort, whose beak is connected with a U-shaped receiver of the same metal, which is cooled and contains a small quantity of water.

The pure acid is a colorless liquid, which boils at 19° (67°F.) and solidifies at -1° (30.2°F.). Sp. gr. 0.985 at 12° (53.6°F.). The aqueous acid is a colorless liquid, highly acid and corrosive, and having a penetrating odor. Great care must be exercised that neither the solution nor the gas come in contact with the skin, as they produce painful ulcers which heal with difficulty, and also constitutional symptoms which may last for days. The inhalation of air containing very small quantities of HF has caused permanent loss of voice, and in two cases, death. When the acid has accidentally come in contact with the skin the part should be washed with dilute solution of potash, and the vesicle which forms should be opened.

Both the gaseous acid and its solution remove the silica from glass, a property utilized in etching upon that substance, the parts upon which no action is desired being protected by a coating of wax.

The presence of fluorin in a compound is detected by reducing the substance to powder, moistening it with sulfuric acid in a platinum crucible, over which is placed a slip of glass prepared as above. At the end of half an hour the wax is removed from the glass, which will be found to be etched if the substance examined contained a fluorid.

CHLORIN.

Symbol=Cl—*Atomic weight*=35.5 (O=16:35.45; H=1:35.17)—*Molecular weight*=71 *Sp. gr.*=2.4502 *A*—*One litre weighs 3.17 grams*—*100 cubic inches weigh 76.3 grains*—*Name derived from* $\chi\lambda\omega\rho\acute{o}s$ = *yellowish green*—*Discovered by Scheele in 1774.*

Occurrence.—Only in combination, most abundantly in sodium chlorid.

Preparation.—(1) By heating together manganese dioxid and hydrochloric acid (Scheele): $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$.

This and similar operations are usually conducted in an apparatus such as that shown in Fig. 29. The earthenware vessel A (which on a small scale may be replaced by a glass flask) is two-thirds filled with lumps of manganese dioxid of the size of hazelnuts and adjusted in the water bath; hydrochloric acid is poured in through the safety-tube and the bath heated. The disengaged gas is caused to bubble through the small quantity of water in B, is then dried by passage over the fragments of calcium chlorid in C, and is finally collected by displacement of air in the vessel D.

When the vessel A has become half filled with liquid it is best to decant the solution of manganous chlorid, wash the remaining oxid with water and begin anew. A kilo of oxid yields 257.5 litres of Cl.

In a modification of this process, which permits of the more easy recovery of the manganese dioxid, nitric acid is used along with

hydrochloric. The reaction is: $2\text{HCl} + 2\text{HNO}_3 + \text{MnO}_2 = \text{Mn}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + \text{Cl}_2$. The MnO_2 and HNO_3 are recovered by heating the manganese nitrate to 190° (374° F.) and treating the vapor with air and steam. The reactions are: $\text{Mn}(\text{NO}_3)_2 = \text{MnO}_2 + \text{N}_2\text{O}_4$ and $\text{N}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{HNO}_3$.

(2) By the action of manganese dioxid upon hydrochloric acid in the presence of sulfuric acid, manganous sulfate being also formed: $\text{MnO}_2 + 2\text{HCl} + \text{H}_2\text{SO}_4 = \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2$. The same quantity of chlorin is obtained as in (1), with the use of half the amount of hydrochloric acid.

(3) By heating a mixture of one part each of manganese dioxid and sodium chlorid, with three parts of sulfuric acid. Hydrochloric

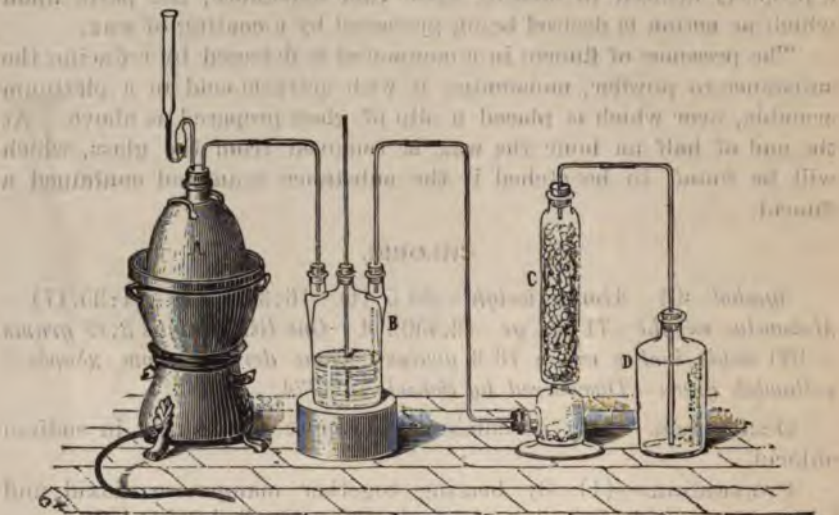


FIG. 29.

acid and sodium sulfate are first formed: $\text{H}_2\text{SO}_4 + 2\text{NaCl} = \text{Na}_2\text{SO}_4 + 2\text{HCl}$; and the acid is immediately decomposed by either of the reactions indicated in (1) and (2), according as sulfuric acid is or is not present in excess.

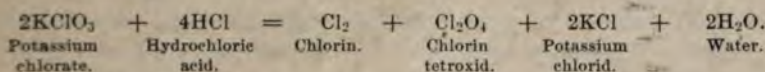
(4) By the action of potassium dichromate upon hydrochloric acid; potassium and chromic chlorids being also formed: $\text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} = 2\text{KCl} + \text{Cr}_2\text{Cl}_6 + 7\text{H}_2\text{O} + 3\text{Cl}_2$. Two parts of powdered dichromate are heated with 17 parts of acid of sp. gr. 1.16; 100 grams of the salt yielding 22.5 litres of Cl .

(5) A convenient method of obtaining chlorin on a laboratory scale is by the use of "chlorin cubes." These are made by pressing together 1 part of plaster of Paris and 4 parts of chlorid of lime (q. v.), cutting into small cubes and drying. The cubes are used in

one of the forms of constant apparatus (Figs. 25, 26, 27), with dilute hydrochloric acid, Cl being evolved at the ordinary temperature.

When a slow evolution of Cl, extending over a considerable period of time, is desired, as for ordinary disinfection, moistened chlorid of lime is exposed to the air, the calcium hypochlorite being decomposed by the atmospheric carbon dioxid. If a more rapid evolution of gas be desired, the chlorid of lime is moistened with dilute hydrochloric acid in place of with water.

(6) By the action of potassium chlorate upon hydrochloric acid Cl is liberated, slowly at the ordinary temperature, more rapidly at the temperature of the water-bath :



(7) Chlorin is obtained industrially in the manufacture of caustic soda by the electrolysis of NaCl.

(8) In Deacon's process cupric oxid is used as a "contact substance" to oxidize hydrochloric acid. The reactions are: $2\text{CuCl}_2 = \text{Cu}_2\text{Cl}_2 + \text{Cl}_2$, then, $\text{Cu}_2\text{Cl}_2 + \text{O}_2 = 2\text{CuO} + \text{Cl}_2$, and, finally, $2\text{CuO} + 4\text{HCl} = 2\text{CuCl}_2 + 2\text{H}_2\text{O}$. As the O is derived from air the Cl obtained is largely diluted with N.

(9) In the Solvay, Weldon and Mond processes Cl is derived from magnesium chlorid by the reaction: $2\text{MgCl}_2 + \text{O}_2 = 2\text{MgO} + 2\text{Cl}_2$.

Properties.—Physical.—A greenish yellow gas, at the ordinary temperature and pressure; it has a penetrating odor, and is, even when highly diluted, very irritating to the respiratory passages. Being soluble in H_2O to the extent of one volume to three volumes of the solvent, it must be collected by displacement of air, as shown in Fig. 29. A saturated aqueous solution of Cl is known to chemists as **chlorin water**, and in pharmacy as **aqua chlori** (U. S.), **Liquor chlori** (Br.). It should bleach, but not redden, litmus paper. Under a pressure of 6 atmospheres at 0° (32° F.), or $8\frac{1}{2}$ atmospheres at 12° (53.6° F.), Cl becomes an oily, yellow liquid, of sp. gr. 1.33; and boiling at -33.6° (-28.5° F.). Liquid chlorin, transported in lead-lined steel cylinders, is now an article of commerce.

Chemical.—Chlorin exhibits a great tendency to combine with other elements, with all of which, except F, O, N, and C, it unites directly, frequently with evolution of light as well as heat, and sometimes with an explosion. With H it combines slowly, to form hydrochloric acid, under the influence of diffuse daylight, and violently in direct sunlight, or in highly actinic artificial lights. A candle burns in Cl with a faint flame and thick smoke, its H combining with the Cl, while carbon becomes free.

At a red heat Cl decomposes H_2O rapidly, with formation of hydrochloric, chloric, and probably hypochlorous acids. The same change takes place slowly under the influence of sunlight, hence chlorin water should be kept in the dark or in bottles of yellow glass.

In the presence of H_2O , chlorin is an active bleaching and disinfecting agent. It acts as an indirect oxidant, decomposing H_2O , the nascent O from which then attacks the coloring or odorous principle.

Chlorin is readily fixed by many organic substances, either by addition or substitution. In the first instance, as when Cl and olefant gas unite to form ethylene chlorid, the organic substance simply takes up two or more atoms of chlorin: $C_2H_4 + Cl_2 = C_2H_4Cl_2$. In the second instance, as when Cl acts upon marsh gas to produce methyl chlorid: $CH_4 + Cl_2 = CH_3Cl + HCl$, each substituted atom of Cl displaces an atom of H, which combines with another Cl atom to form hydrochloric acid.

Hydrogen Chlorid — Hydrochloric Acid — Muriatic Acid — Acidum Hydrochloricum (U. S.; Br.)— HCl —*Molecular weight* = 36.5—*Sp. gr.* 1.259 *A*—*A litre weighs* 1.6293 gram.

Occurrence.—In volcanic gases and in the gastric juice of the mammalia.

Preparation.—(1) By the direct union of its constituent elements.

(2) By the action of sulfuric acid upon a chlorid, a sulfate being at the same time formed: $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl$.

This is the reaction by which the HCl used in the arts is produced.

(3) Hydrochloric acid is also formed in a great number of reactions, as when Cl is substituted in an organic compound.

Properties.—*Physical.*—A colorless gas, acid in reaction and taste, having a sharp, penetrating odor, and producing great irritation when inhaled. It becomes liquid under a pressure of 40 atmospheres at 4° (39.2° F.) Its critical temperature is 52° (125.6° F.) and its critical pressure 83 atmospheres. It is very soluble in H_2O , one volume of which dissolves 480 volumes of the gas at 0° (32° F.)

Chemical.—Hydrochloric acid is neither combustible nor a supporter of combustion, although certain elements, such as K and Na, burn in it. It forms white clouds on contact with moist air.

Solution of Hydrochloric Acid.—It is in the form of aqueous solution that this acid is usually employed in the arts and in pharmacy. It is, when pure, a colorless liquid (yellow when impure), acid in taste and reaction, whose sp. gr. and boiling-point vary with the degree of concentration. When heated, it evolves HCl , if it contain more than 20 per cent. of that gas, and H_2O if it con-

tain less. A solution containing 20 per cent. boils at 111° (232° F.), is of sp. gr. 1.099, has the composition $\text{HCl} + 8\text{H}_2\text{O}$, and distills unchanged.

Commercial muriatic acid is a yellow liquid; sp. gr. about 1.16; contains 32 per cent. HCl ; and contains ferric chlorid, sodium chlorid; and arsenical compounds.

Acidum hydrochloricum is a colorless liquid, containing small quantities of impurities. It contains 31.9 per cent. HCl and its sp. gr. is 1.16 (U. S.; Br.) The dilute acid is the above diluted with water. Sp. gr. 1.049 = 10 per cent. HCl (U. S.); sp. gr. 1.052 = 10.5 per cent. HCl (Br.)

O. P. (chemically pure) acid is usually the same as the strong pharmaceutical acid and far from pure (see below). The strongest solution has a sp. gr. of 1.20 and contains 40.8 per cent. HCl .

Hydrochloric acid is classed, along with nitric and sulfuric acids, as one of three **strong mineral acids**. It is decomposed by many elements, with formation of a chlorid and liberation of hydrogen: $2\text{HCl} + \text{Zn} = \text{ZnCl}_2 + \text{H}_2$. With oxids and hydroxids of the metals it enters into double decomposition, forming H_2O and a chlorid: $\text{CaO} + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O}$ or $\text{CaH}_2\text{O}_2 + 2\text{HCl} = \text{CaCl}_2 + 2\text{H}_2\text{O}$.

Oxidizing agents decompose HCl with liberation of Cl . A mixture of hydrochloric and nitric acids in the proportion of three molecules of the former to one of the latter (18 cc. HNO_3 : 82 cc. HCl soln.), is the **acidum nitrohydrochloricum** (U. S.; Br.), or **aqua regia**. The latter name alludes to its power of dissolving gold, by combination of the nascent Cl , which it liberates, with that metal. to form the soluble auric chlorid (p. 193).

Impurities.—A chemically pure solution of this acid is exceedingly rare. The impurities usually present are: *Sulfurous acid*—hydrogen sulfid is given off when the acid is poured upon zinc; *Sulfuric acid*—a white precipitate is formed with barium chlorid; *Chlorin* colors the acid yellow; *Lead* gives a black color when the acid is treated with hydrogen sulfid; *Iron*—the acid gives a red color with ammonium thiocyanate; *Arsenic*—the method of testing by hydrogen sulfid is not sufficient. If the acid is to be used for toxicological analysis, a litre, diluted with half as much H_2O , and to which a small quantity of potassium chlorate has been added, is evaporated over the water bath to 400 cc.; 25 cc. of sulfuric acid are then added, and the evaporation continued until the liquid measures about 100 cc. This is introduced into a Marsh apparatus and must produce *no* mirror during an hour.

Chlorids.—A few of the chlorids are liquid, SnCl_4 , SbCl_5 ; the remainder are solid, crystalline and more or less volatile. The metallic chlorids are soluble in water, except AgCl and Hg_2Cl_2 , which

are insoluble, and PbCl_2 , and Cu_2Cl_2 , which are sparingly soluble. The chlorids of the non-metals are decomposed by H_2O .

The chlorids are formed: (1) By the direct union of the elements: $\text{P} + \text{Cl}_5 = \text{PCl}_5$; (2) By the action of chlorine upon a heated mixture of oxid and carbon: $\text{Al}_2\text{O}_3 + 3\text{C} + 3\text{Cl}_2 = \text{Al}_2\text{Cl}_6 + 3\text{CO}$; (3) By solution of the metal, oxid, hydroxid, or carbonate in HCl : $\text{Zn} + 2\text{HCl} = \text{ZnCl}_2 + \text{H}_2$; (4) By double decomposition between a solution of a chlorid and that of another salt whose metal forms an insoluble chlorid: $\text{AgNO}_3 + \text{NaCl} = \text{AgCl} + \text{NaNO}_3$.

Chloridion—Analytical Characters.—Solutions of hydrochloric acid and of chlorids contain the ion, chloridion Cl' , which gives the following reactions: (1) With AgNO_3 a white, flocculent ppt., insol. in HNO_3 , sol. in NH_4HO . (2) With $\text{Hg}_2(\text{NO}_3)_2$, a white ppt., which turns black with NH_4HO .

Toxicology.—Poisons and Corrosives.—*A poison is any substance which, being in solution in, or acting chemically upon the blood, may produce death or serious bodily harm.*

A corrosive is a substance capable of producing death by its chemical action upon a tissue with which it comes in direct contact.

The corrosives act much more energetically when concentrated than when dilute; and when the dilution is great they have no deleterious action. The degree of concentration in which the true poisons are taken is of little influence upon their action.

Under the above definitions the strong mineral acids act as corrosives rather than as poisons. They produce their injurious results by destroying the tissues with which they come in contact, and will cause death as surely by destroying a large surface of skin as when they are taken into the stomach.

The symptoms of corrosion by the mineral acids begin immediately, during the act of swallowing. The chemical action of the acid upon every part with which it comes in contact causes acute burning pain, extending from the mouth to the stomach and intestine, referred chiefly to the epigastrium. Violent and distressing vomiting of dark, tarry, or "coffee-ground," highly acid material is a prominent symptom. Eschars, at first white or gray, later brown or black, are formed where the acid has come in contact with the skin or mucous membrane. Respiration is labored and painful, partly by pressure of the abdominal muscles, but also, in the case of hydrochloric acid, from entrance of the irritating gas into the respiratory passages. Death may occur within twenty-four hours, from collapse; more suddenly from perforation of large blood-vessels, or from peritonitis; or after several weeks, secondarily, from starvation, due to closure of the pylorus by inflammatory thickening, and destruction of the gastric glands.

The object of the treatment in corrosion by the mineral acids is to neutralize the acid and convert it into a harmless salt. For this purpose the best agent is magnesia (magnesia usta), suspended in a small quantity of water, or if this be not at hand, a strong solution of soap. Chalk and the carbonates and bicarbonates of sodium and potassium should not be given, as they generate large volumes of gas. The serapings of a plastered wall, or oil, are entirely useless. Any attempt at the introduction of a tube into the œsophagus is attended with danger of perforation, except in the earliest stages of the intoxication.

Compounds of Chlorin and Oxygen.—Two compounds of chlorin and oxygen are known. They are both very unstable, and prone to sudden and violent decomposition.

Chlorin Monoxid.— Cl_2O —87—*Hypochlorous anhydrid* or *oxid*, is formed by the action, below 20° (68° F.), of dry Cl upon precipitated mercuric oxid: $\text{HgO} + 2\text{Cl}_2 = \text{HgCl}_2 + \text{Cl}_2\text{O}$.

On contact with H_2O it forms **hypochlorous acid**, HClO , which owing to its instability, is not used industrially, although the hypochlorites of Ca, K, and Na are.

Chlorin Tetroxid—*Chlorin peroxid*, Cl_2O_4 —135—is a violently explosive body, produced by the action of sulfuric acid upon potassium chlorate. Below -20° (-4° F.) it is an orange-colored liquid; above that temperature a yellow gas. It explodes violently when heated to a temperature below 100° (212° F.). There is no corresponding hydrate known, and if it be brought in contact with an alkaline hydroxid, a mixture of chlorate and chlorite is formed.

Besides the above, two oxacids of Cl are known, the anhydrids corresponding to which have not been isolated.

Chloric Acid— HClO_3 —84.5—obtained, in aqueous solution, as a strongly acid, yellowish, syrupy liquid, by decomposing its barium salt by the proper quantity of sulfuric acid.

Perchloric Acid— HClO_4 —100.5—is the most stable of the series. It is obtained by boiling potassium chlorate with hydrofluosilicic acid, decanting the cold fluid, evaporating until white fumes appear, decanting from time to time, and finally distilling. It is a colorless, oily liquid; sp. gr. 1.782; which explodes on contact with organic substances or charcoal.

BROMIN.

Bromum, U. S., Br.—*Symbol*=Br.—*Atomic weight*=80—(O=16: 79.96; H=1: 79.36)—*Molecular weight*=160—*Sp. gr. of liquid*=3.1872 at 0° ; *of vapor*=5.52 A—*Freezing point*= -24.5° (-12.1° F.)—*Boiling point*= 63° (145.4° F.)—*Name derived from βρῶμος*=a stench—*Discovered by Balard in 1826.*

Occurrence.—Only in combination, most abundantly with Na and Mg in sea water and the waters of mineral springs.

Preparation.—It is obtained from the mother liquors, left by the evaporation of sea water, and of that of certain mineral springs, and from sea weed. These are mixed with sulfuric acid and manganese dioxid and heated, when the bromids are decomposed by the Cl produced, and Br distils.

Properties.—*Physical.*—A dark reddish-brown liquid, volatile at all temperatures above -24.5° (-12.1° F.); giving off brown-red vapors which produce great irritation when inhaled. Soluble in water to the extent of 3.2 parts per 100 at 15° (59° F.); more soluble in alcohol, carbon disulfid, chloroform, and ether.

Chemical.—The chemical characters of Br are similar to those of Cl, but less active.—With H_2O it forms a crystalline hydrate at 0° (32° F): $Br \cdot 5H_2O$. Its aqueous solution is decomposed by exposure to light, with formation of hydrobromic acid.

It is highly poisonous.

Hydrogen Bromid—Hydrobromic acid—Acidum hydrobromicum dil. (U. S.)= HBr —*Molecular weight*=81—*Sp. gr.*=2.71
A—A litre weighs 3.63 grams—Liquefies at -69° ($-92^{\circ}.2$ F.)—Solidifies at -73° (-99.4° F.).

Preparation.—This substance cannot be obtained from a bromid as HCl is obtained from a chlorid. It is produced, along with phosphorous acid, by the action of H_2O upon phosphorus tribromid: $PBr_3 + 3H_2O = H_3PO_3 + 3HBr$; or by the action of Br upon paraffin.

Properties.—A colorless gas; produces white fumes with moist air; acid in taste and reaction, and readily soluble in H_2O , with which it forms a hydrate, $HBr \cdot 2H_2O$. Its chemical properties are similar to those of HCl .

Bromids closely resemble the chlorids and are formed under similar conditions. They are decomposed by chlorin, with formation of a chlorid and liberation of Br: $2KBr + Cl_2 = 2KCl + Br_2$. The metallic bromids are soluble in H_2O , except $AgBr$ and Hg_2Br_2 , which are insoluble, and $PbBr_2$, which is sparingly soluble. The bromids of Mg, Al, Ca are decomposed into oxid and HBr on evaporation of their aqueous solutions.

Bromidion—Analytical Characters.—Solutions of hydrobromic acid and of bromids contain the anion Br' , which gives the following reactions: (1) With $AgNO_3$, a yellowish white ppt., insoluble in HNO_3 , sparingly soluble in NH_4HO . (2) With chlorin water a yellow solution which communicates the same color to chloroform and to starch-paste.

Hypobromous Acid— HBrO —97—is obtained, in aqueous solution, by the action of Br upon mercuric oxid, silver oxid, or silver nitrate. When Br is added to concentrated solution of potassium hydroxid no hypobromite is formed, but a mixture of bromate and bromid, having no decolorizing action. With sodium hydroxid, however, sodium hypobromite is formed in solution; and such a solution, freshly prepared, is used in Knop's process for determining urea (q. v.).

Bromic Acid— HBrO_3 —129—has only been obtained in aqueous solution, or in combination. It is formed by decomposing barium bromate with an equivalent quantity of sulfuric acid: $\text{Ba}(\text{BrO}_3)_2 + \text{H}_2\text{SO}_4 = 2\text{HBrO}_3 + \text{BaSO}_4$. In combination it is produced, along with the bromid, by the action of Br on caustic potassa: $3\text{Br}_2 + 6\text{KHO} = \text{KBrO}_3 + 5\text{KBr} + 3\text{H}_2\text{O}$.

Perbromic Acid— HBrO_4 —145—is obtained as a comparatively stable, oily liquid, by the decomposition of perchloric acid by Br, and concentrating over the water-bath.

IODIN.

Iodum (U. S.; Br.)—*Symbol*=I—*Atomic weight*=127 (O=16: 126.97; H=1:126.01)—*Molecular weight*=254—*Sp. gr. of solid*=4.948; *of vapor*=8.716 A—*Fuses at* 113.6° (236.5° F.)—*Boils at* 175° (347° F.)—*Name derived from* *ιώδης*=violet—*Discovered by Courtois in* 1811.

Occurrence.—In combination with Na, K, Ca, and Mg, in seawater, the waters of mineral springs, marine plants and animals. Cod-liver oil contains about 37 parts in 100,000.

Preparation.—It is obtained from the ashes of sea-weed, called *kelp* or *varech*. These are extracted with H_2O , and the solution evaporated to small bulk. The mother liquor, when separated from the other salts which crystallize out, contains the iodids, which are decomposed by Cl, aided by heat, and the liberated iodin is condensed.

Properties.—*Physical.*—Blue-gray, crystalline scales, having a metallic luster. Volatile at all temperatures, the vapor having a violet color and a peculiar odor. The density of vapor of iodin, at one atmosphere of pressure and at temperatures between its boiling point and about 500° is 254 (O=32), corresponding to the molecular formula I_2 (p. 56), but above that temperature the density diminishes, until at 1,500° it has fallen to 127, corresponding to the molecular formula I, where it remains constant. Molecular iodine is, therefore, dissociated by heat (p. 90). Iodine is very sparingly soluble in water, but the aqueous solution, standing over excess of iodine, con-

tinues to dissolve it by reason of the formation of hydriodic acid. Solutions of hydriodic acid and of metallic iodids dissolve notably larger quantities of iodine than does pure water, probably because of the formation of the ion I_3' . Iodine is very soluble in alcohol, ether, chloroform, benzene and carbon bisulfid. With the three last named solvents the solutions are violet, with others brown in color.

Chemical.—In its chemical characters I resembles Cl and Br, but is less active. It decomposes H_2O slowly and is a weak bleaching and oxidizing agent. In presence of water, it decomposes hydrogen sulfid with formation of hydriodic acid, and liberation of sulfur. It does not combine directly with oxygen, but does with ozone. Potassium hydroxid solution dissolves it, with formation of potassium iodid, and some hypoiodite. Nitric acid oxidizes it to iodic acid. With ammonium hydroxid solution it forms the explosive nitrogen iodid.

Toxicology.—Taken internally, iodine acts both as a local irritant and as a true poison. It is discharged as an alkaline iodid by the urine and perspiration, and when taken in large quantity it appears in the feces.

The poison should be removed as rapidly as possible by the use of the stomach pump and of emetics. Farinaceous substances may also be given.

Hydrogen Iodid—Hydriodic acid—HI—Molecular weight=127.85—Sp. gr. 4.443 A.

Preparation.—By the decomposition of phosphorus triiodid by water: $PI_3 + 3H_2O = H_3PO_3 + 3HI$. Or, in solution by passing hydrogen sulfid through water holding iodine in suspension: $H_2S + I_2 = 2HI + S$.

Properties.—A colorless gas, forming white fumes on contact with air, and of strongly acid reaction. Under the influence of cold and pressure it forms a yellow liquid, which solidifies at -55° (-67° F.). Water dissolves it to the extent of 425 volumes for each volume of the solvent at 10° (50° F.).

It is partly decomposed into its elements by heat. Mixed with O it is decomposed, even in the dark, with formation of H_2O and liberation of I. Under the influence of sunlight the gas is slowly decomposed, although its solutions are not so affected, if they be free from air. Chlorine and bromine decompose it, with liberation of iodine. With many metals it forms iodids. It yields up its H readily and is used in organic chemistry as a source of that element in the nascent state.

Iodids are formed under the same conditions as the chlorids and bromids, which they resemble in their properties. The metallic iodids

are soluble in water—except AgI , Hg_2I_2 , which are insoluble, and PbI_2 , which is very slightly soluble. The iodids of the earth metals are decomposed into oxid and HI on évaporation of their aqueous solutions. Chlorin decomposes the iodids as it does the bromids.

Iodidion—Analytical Characters.—Solutions of hydriodic acid or of iodids contain iodidion, I' , which forms a yellow ppt., insol. in HNO_3 and in NH_4HO , with $\text{Ag}\cdot\text{NO}_3$. Brown solutions of excess of iodine in HI or KI contain triiodidion, I_3' , which, as iodine is removed from the solution, is decomposed into $\text{I}' + \text{I}_2$. Aqueous or alcoholic solutions of free iodine, not of iodidion, color starch paste dark blue or black, and chloroform or carbon bisulfid violet. The same colors are produced with solutions of iodids after liberation from them of free iodine by fuming HNO_3 or chlorin water. At about 100° starch iodid is dissociated and decolorized, the color returning on cooling.

Chlorids of Iodine.—Chlorine and iodine combine with each other in two proportions: **Iodine monochlorid**, or **protochlorid**— ICl is a red-brown, oily, pungent liquid, formed by the action of dry Cl upon I , and distilling at 100° (212°F.). **Iodine trichlorid**, or **perchlorid**— ICl_3 is a yellow, crystalline solid, having an astringent, acid taste and a penetrating odor; very volatile; its vapor irritating; easily soluble in water. It is formed by saturating H_2O holding I in suspension with Cl , and adding concentrated sulfuric acid. ICl_3 has been used as an antiseptic.

Oxacids of Iodine.—The best known of these are the highest two of the series—iodic and periodic acids.

Iodic Acid— HIO_3 —176.85 is formed as an iodate, whenever I is dissolved in a solution of an alkaline hydroxid: $\text{I}_2 + 6\text{KHO} = \text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{O}$. As the free acid, by the action of strong oxidizing agents, such as nitric acid, or chloric acid, upon I ; or by passing Cl for some time through H_2O holding I in suspension.

Iodic acid appears in white crystals, decomposable at 170° (338°F.), and quite soluble in H_2O , the solution having an acid reaction, and a bitter, astringent taste.

It is an energetic oxidizing agent, yielding up its O readily, with separation of elementary I or of HI . It is used as a test for the presence of morphin (*q. v.*).

Periodic Acid— HIO_4 —191.85—is formed by the action of Cl upon an alkaline solution of sodium iodate. The sodium salt thus obtained is dissolved in nitric acid, treated with silver nitrate, and the resulting silver periodate is then decomposed with H_2O . From the solution the acid is obtained in colorless crystals, fusible at 130° (266°F.), very soluble in water, and readily decomposable by heat.

II. SULFUR GROUP.

SULFUR. SELENIUM. TELLURIUM.

The elements of this group are bivalent in most of their compounds, in some they are quadrivalent or hexavalent. With hydrogen they form compounds composed of one volume of the element, in the form of vapor, with two volumes of hydrogen—the combination being attended with a condensation in volume of one-third. Mineral acids in which they occur are dibasic. They are all solids at ordinary temperatures. The relation of their compounds to each other is shown in the following table:

H_2S	SO_2	SO_3	H_2SO_2	H_2SO_3	H_2SO_4
H_2Se	SeO_2	SeO_3	—	H_2SeO_3	H_2SeO_4
H_2Te	TeO_2	TeO_3	—	H_2TeO_3	H_2TeO_4
Hydro-le acid.	Dioxid.	Trioxid.	Hypo-ous acid.	-ous acid.	-ic acid.

SULFUR.

Symbol = S — *Atomic weight* = 32 (O = 16:32.06; H = 1:31.8) — *Molecular weight* = 64 — *Sp. gr. of vapor* = 2.22 A — *Fuses at* 114° (237.2° F.) — *Boils at* 447.3° (837° F.).

Occurrence. — Free in crystalline powder, large crystals, or amorphous, in volcanic regions. In combination in sulfids and sulfates, and in protein substances.

Preparation. — By purification of the native sulfur or decomposition of *pyrites*, natural sulfids of iron.

Crude sulfur is the product of the first distillation. A second distillation, in more perfectly constructed apparatus, yields *refined sulfur*. During the first part of the distillation, while the air of the condensing chamber is still cool, the vapor of S is suddenly condensed into a fine, crystalline powder, which is **flowers of sulfur**, **sulfur sublimatum** (*U. S.*). Later, when the temperature of the condensing chamber is above 114°, the liquid S collects at the bottom, whence it is drawn off and cast into sticks of **roll sulfur**.

Properties. — *Physical.* — Sulfur is usually yellow in color. At low temperature, and in minute subdivision, as in the precipitated **milk of sulfur**, **sulfur præcipitatum** (*U. S.*), it is almost or quite colorless. Its taste and odor are faint but characteristic. At 114° (237.2° F) it fuses to a thin yellow liquid, which at 150°–160° (302°–320° F.) becomes thick and brown; at 330°–340° (626–642.2° F.) it again becomes thin and light in color; finally it boils, giving off brownish yellow vapor at a temperature variously stated

between 440° (824° F.) and 448° (838.4° F.). If heated to about 400° (752° F.) and suddenly cooled, it is converted into **plastic sulfur**, which may be moulded into any desired form. It is insoluble in water, sparingly soluble in anilin, phenol, benzene, petroleum ether, and chloroform; readily soluble in sulfur chlorid, S_2Cl_2 , and carbon disulfid. It dissolves in hot alcohol, and crystallizes from the solution, on cooling, in white prismatic crystals. It is dimorphous. When fused sulfur crystallizes it does so in oblique rhombic prisms. Its solution in carbon disulfid deposits it on evaporation in rhombic octahedra. The prismatic variety is of sp. gr. 1.95 and fuses at 120° (248° F.); the sp. gr. of the octahedral is 2.05 and its fusing point 114.5° (238° F.). The prismatic crystals, by exposure to air, become opaque, by reason of a gradual conversion into octahedra.

Chemical.—Sulfur unites readily with other elements, especially at high temperatures. Heated in air or O, it burns with a blue flame to sulfur dioxid, SO_2 . In H it burns with formation of hydrogen sulfid, H_2S . The compounds of S are similar in constitution, and to some extent in chemical properties, to those of O. In many organic substances S may replace O, as in thiocyanic acid, $CNSH$, corresponding to cyanic acid, $CNOH$. Such compounds are designated by the syllable *thio*; the syllable *sulfo*, in the name of a compound, indicates that it contains the bivalent group, SO_2 .

Sulfur is used principally in the manufacture of gunpowder; also to some extent in making sulfuric acid, sulfur dioxid, and matches, and for the prevention of fungoid and parasitic growths.

Hydrogen Monosulfid—Sulphydric acid—Hydrosulfuric acid—Sulfuretted hydrogen— H_2S —Molecular weight=34—Sp. gr.=1.19 A.

Occurrence.—In volcanic gases; as a product of the decomposition of organic substances containing S; in solution, in the waters of some mineral springs; and, occasionally, in small quantity, in the gases of the intestine. It is produced from proteins and other organic substances containing S by microbic action (sulphydric fermentation).

Preparation.—(1) By direct union of the elements; either by burning S in H, or by passing H through molten S.

(2) By the action of nascent H upon sulfuric acid, if the mixture become heated. (See Marsh test for arsenic.)

(3) By the action of HCl upon antimony trisulfid: $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$.

(4) By the action of dilute sulfuric acid upon ferrous sulfid: $FeS + H_2SO_4 = FeSO_4 + H_2S$. This is the method generally used. The gas should be purified by passage over dry calcium chlorid, then through a tube, 20 cent. long, loosely filled with solid iodine, and,

finally, through a solution of potassium sulfid. The purpose of the iodine is to arrest traces of hydrogen arsenid, which may be present.

(5) By the action of HCl upon calcium sulfid: $\text{CaS} + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{S}$.

Properties.—*Physical.*—A colorless gas having the odor of rotten eggs and a disgusting taste; soluble in H_2O to the extent of 3.23 parts to 1 at 15° (59° F.); soluble in alcohol. Under 17 atmospheres pressure, or at -74° (-101.2° F.) at the ordinary pressure, it liquefies; at -85.5° (-122° F.) it forms white crystals.

Chemical.—Burns in air with formation of sulfur dioxid and water: $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O}$. If the supply of oxygen be deficient, H_2O is formed, and sulfur liberated: $2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + \text{S}_2$. Mixtures of H_2S and air or O explode on contact with flame. Solutions of the gas when exposed to air become oxidized with deposition of S. Such solutions should be made with boiled H_2O , and kept in bottles which are completely filled, and well corked. Oxidizing agents, Cl, Br, and I remove its H with deposition of S. Hydrogen sulfid and sulfur dioxid mutually decompose each other into water, pentathionic acid and sulfur: $4\text{SO}_2 + 3\text{H}_2\text{S} = 2\text{H}_2\text{O} + \text{H}_2\text{S}_5\text{O}_6 + \text{S}_2$.

When the gas is passed through a solution of an alkaline hydroxid its S displaces the O of the hydroxid to form a sulphydrate: $\text{H}_2\text{S} + \text{KHO} = \text{H}_2\text{O} + \text{KHS}$. With solutions of metallic salts H_2S usually relinquishes its S to the metal: $\text{CuSO}_4 + \text{H}_2\text{S} = \text{CuS} + \text{H}_2\text{SO}_4$, a property which renders it of great value in analytical chemistry.

Physiological.—Hydrogen sulfid is produced in the intestine by the decomposition of protein substances or of taurochloric acid; it also occurs sometimes in abscesses, and in the urine in tuberculosis, variola, and cancer of the bladder. It may also reach the bladder by diffusion from the rectum.

Toxicology.—An animal dies almost immediately in an atmosphere of pure H_2S , and the diluted gas is still rapidly fatal. An atmosphere containing 1 per cent may be fatal to man, although individuals habituated to its presence can exist in an atmosphere containing 3 per cent. Even when highly diluted it produces a condition of low fever, and care is to be taken that the air of laboratories in which it is used shall not become contaminated with it. Its toxic powers are due primarily, if not entirely, to its power of reducing and combining with the blood-coloring matter.

The form in which hydrogen sulfid generally produces deleterious effects is as a constituent of the gases emanating from sewers, privies, burial vaults, etc. These give rise to either slow poisoning, as when sewer gases are admitted to sleeping and other apartments by defective plumbing, or to sudden poisoning, as when a person enters a vault or other locality containing the noxious atmosphere.

The treatment should consist in promoting the inhalation of pure air, artificial respiration, cold affusions, and the administration of stimulants.

After death the blood is found to be dark in color, and gives the spectrum shown in Fig. 30, due to sulfhæmoglobin.

Sulfids and Hydrosulfids.—These compounds bear the same relation to sulfur that the oxids and hydroxids do to oxygen. The two sulfids of arsenic, As_2S_3 and As_2S_5 , correspond to the two oxids, As_2O_3 and As_2O_5 , and the potassium hydrosulfid, KHS , corresponds to the hydroxid, KHO .

Many metallic sulfids occur in nature, and are important ores of the metals, as the sulfids of zinc, mercury, cobalt, nickel, and iron. They are formed artificially, either by direct union of the elements at elevated temperatures, as in the case of iron: $\text{Fe} + \text{S} = \text{FeS}$; or by reduction of the corresponding sulfate, as in the case of calcium: $\text{CaSO}_4 + 2\text{C} = \text{CaS} + 2\text{CO}_2$.

The sulfids are insoluble in H_2O , except those of the alkali metals. Many of the sulfids are soluble in alkaline liquids, and behave as



FIG. 30

thio-anhydrids, forming thio-salts, corresponding to the oxysalts. Thus potassium arsenate, K_3AsO_4 , and thioarsenate, K_3AsS_4 ; antimonate, K_3SbO_4 , and thioantimonate, K_3SbS_4 .

The metallic sulfids are decomposed when heated in air, usually with the formation of sulfur dioxide and the metallic oxid; sometimes with the formation of the sulfate; and sometimes with the liberation of the metal, and the formation of sulfur dioxide. The strong mineral acids decompose the sulfids with formation of hydrogen monosulfid.

Analytical Characters.—*Hydrogen Sulfid.*—(1) Blackens paper moistened with lead acetate solution. (2) Has an odor of rotten eggs.

Sulfids.—(1) Heated in the oxidizing flame of the blowpipe, give a blue flame and odor of SO_2 . (2) With a mineral acid give off H_2S (except sulfids of Hg , Au , and Pt).

Hydrogen Polysulfids.—Several other compounds of S and H , corresponding to the polysulfids of K , Na , and Ca , are known. The most stable is hydrogen pentasulfid, H_2S_5 , which can only exist in the absence of water and at low temperatures.

Sulfur and the Halogens.—But one compound of S and Cl exists: Sulfurous chlorid, S_2Cl_2 , formed when S is distilled in an atmosphere of Cl. It is a yellow, fuming liquid, used as a solvent for S. Several oxychlorids are also known.

Bromin in contact with excess of S forms a red liquid which consists principally of S_2Br_2 .

The iodid, S_2I_2 , is obtained by heating together 32 parts S and 127 parts I. It is a steel-gray, crystalline substance, fusible at 60° (140° F.), insoluble in water; and has been used in medicine.

Sulfur Dioxid.—*Sulfurous oxid*, or *anhydrid*—**Acidum sulfurosum** (U. S. ; Br.)— SO_2 —*Molecular weight*=64—*Sp. gr. of gas*=2.213 ; *of liquid*=1.45—*Boils at* -10° (14° F.); *solidifies at* -75° (-103° F.).

Occurrence.—In volcanic gases and in solution in some mineral waters.

Preparation.—(1) By burning S in air or O.

(2) By roasting iron pyrites in a current of air.

(3) During the combustion of coal or coal-gas containing S or its compounds.

(4) By heating sulfuric acid with copper: $2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2$.

(5) By heating sulfuric acid with charcoal: $2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O$.

(6) By decomposing calcium sulfite, made into cubes with plaster of Paris, by HCl, at the ordinary temperature.

When the gas is to be used as a disinfectant it is usually obtained by reaction (1); in sulfuric acid factories (2) is used; (3) indicates the method in which atmospheric SO_2 is chiefly produced; in the laboratory (4) and (6) are used; (5) is the process directed by the U. S. and Br. Pharmacopœias.

Properties.—*Physical.*—A colorless, suffocating gas, having a disagreeable and persistent taste. Very soluble in H_2O , which at 15° (59° F.) dissolves about 40 times its volume (see below); also soluble in alcohol. At -10° (14° F.) it forms a colorless, mobile, transparent liquid, by whose rapid evaporation a cold of -65° (-85° F.) is obtained. Liquid SO_2 packed in sealed tins or in syphons, is now a commercial article.

Chemical. Sulfur dioxid is neither combustible nor a supporter of combustion. Heated with H it is decomposed: $SO_2 + 2H_2 = S + 2H_2O$. With nascent hydrogen, H_2S is formed: $SO_2 + 3H_2 = H_2S + 2H_2O$.

Water not only dissolves the gas, but combines with it to form the true sulfurous acid, H_2SO_3 . With solutions of metallic hydroxids it forms metallic sulfites: $SO_2 + KHO = KHSO_3$; or $SO_2 + 2KHO =$

$K_2SO_3 + H_2O$. A hydrate having the composition $H_2SO_3 \cdot 8H_2O$ has been obtained as a crystalline solid, fusible at $+4^\circ$ (39.2° F.).

Sulfur dioxide and sulfurous acid solution are powerful reducing agents, being themselves oxidized to sulfuric acid: $SO_2 + H_2O + O = H_2SO_4$; or $H_2SO_3 + O = H_2SO_4$. It reduces nitric acid with formation of sulfuric acid and nitrogen tetroxide: $SO_2 + 2HNO_3 = H_2SO_4 + N_2O_4$. It decolorizes organic pigments, without, however, destroying the pigment, whose color may be restored by an alkali or a stronger acid. It destroys H_2S , acting, in this instance, not as a reducing but as an oxidizing agent: $4SO_2 + 3H_2S = 2H_2O + H_2S_3O_6 + S_2$. With Cl it combines directly under the influence of sunlight to form **sulfuryl chloride** (SO_2) Cl_2 .

Analytical Characters.—(1) Odor of burning sulfur.

(2) Paper moistened with starch paste and iodic acid solution turns blue in air containing 1 in 3,000 of SO_2 .

Sulfur Trioxide—*Sulfuric oxid or anhydride*— SO_3 —*Molecular weight* = 80—*Sp. gr.* 1.95.

Preparation.—(1) By union of SO_2 and O at 250° – 300° (482° – 572° F.) or in presence of spongy platinum.

(2) By heating sulfuric acid in presence of phosphoric anhydride: $H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$.

(3) By heating dry sodium pyrosulfate: $Na_2S_2O_7 = Na_2SO_4 + SO_3$.

(4) By heating pyrosulfuric acid below 100° (212° F.), in a retort fitted with a receiver, cooled by ice and salt: $H_2S_2O_7 = H_2SO_4 + SO_3$.

Properties.—White, silky, odorless crystals which give off white fumes in damp air. It unites with H_2O with a hissing sound, and elevation of temperature, to form sulfuric acid. When dry it does not redden litmus.

Sulfur trioxide exists in two isomeric (see isomerism) modifications, being one of the few instances of isomerism among mineral substances. The α modification, liquid at summer temperature, solidifies in colorless prisms at 16° (60.8° F.) and boils at 46° (114.8° F.). The β isomere is a white, crystalline solid which gradually fuses and passes into the α form at about 50° (122° F.)

Oxacids of Sulfur.

H_2SO_2 Hyposulfurous acid.

H_2SO_3 Sulfurous acid.

H_2SO_4 Sulfuric acid.

$H_2S_2O_8$ Persulfuric acid.

$H_2S_2O_3$ Thiosulfuric acid.

$H_2S_2O_7$ Pyrosulfuric acid.

$H_2S_2O_6$ Dithionic acid.

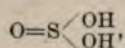
$H_2S_3O_6$ Trithionic acid.

$H_2S_4O_6$ Tetrathionic acid.

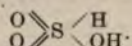
$H_2S_5O_6$ Pentathionic acid.

Hyposulfurous Acid— H_2SO_2 —66.—*Hydrosulfurous acid*—Is an unstable body known only in solution, obtained by the action of zinc upon solution of sulfurous acid. It is a powerful bleaching and de-oxidizing agent.

Sulfurous Acid— H_2SO_3 —82.—Although sulfurous acid has not been isolated, it, in all probability, exists in the acid solution, formed when sulfur dioxid is dissolved in water: $\text{SO}_2 + \text{H}_2\text{O} = \text{SO}_3\text{H}_2$. Its salts, the sulfites, are well defined. From the existence of certain organic derivatives (see sulfonic acids) it would seem that two isomeric modifications of the acid may exist. They are distinguished as the *symmetrical*, in which the S atom is quadrivalent.



and the *unsymmetrical*, in which the S atom is hexavalent.



Sulfites.—The sulfites are decomposed by the stronger acids, with evolution of sulfur dioxid. Nitric acid oxidizes them to sulfates. The sulfites of the alkali metals are soluble, and are active reducing agents.

The analytical characters of the sulfites (sulfosion) are: (1) With HCl they give off SO_2 . (2) With zinc and HCl they give off H_2S . (3) With AgNO_3 they form a white ppt., soluble in excess of sulfite, and depositing metallic Ag when the mixture is boiled. (4) With $\text{Ba}(\text{NO}_3)_2$ they form a white ppt., soluble in HCl. If chlorine water be added to the solution so formed a white ppt., insoluble in acids, is produced.

Sulfuric Acid—Oil of Vitriol—Acidum sulfuricum (U. S.; Br.)— H_2SO_4 —98.

Preparation.—(1) By the union of sulfur trioxid and water: $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$.

(2) By the oxidation of SO_2 or of S in the presence of water: $2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{H}_2\text{SO}_4$; or $\text{S}_2 + 2\text{H}_2\text{O} + 3\text{O}_2 = 2\text{H}_2\text{SO}_4$.

The manufacture of H_2SO_4 may be said to be the basis of all chemical industry, as there are but few processes in chemical technology into some part of which it does not enter. The method followed at present, the result of gradual improvement, may be divided into two stages: (1) the formation of a dilute acid; (2) the concentration of this product.

The first part is carried on in immense chambers of timber, lined with lead, and furnishes an acid having a sp. gr. of 1.55, and containing 65 per cent of true sulfuric acid, H_2SO_4 . Into these chambers SO_2 , obtained by burning sulfur, or by roasting pyrites, is

driven, along with a large excess of air. In the chambers it comes in contact with nitric acid, at the expense of which it is oxidized to H_2SO_4 , while nitrogen tetroxid (red fumes) is formed: $\text{SO}_2 + 2\text{HNO}_3 = \text{H}_2\text{SO}_4 + \text{N}_2\text{O}_4$. Were this the only reaction, the disposal of the red fumes would present a serious difficulty and the amount of nitric acid consumed would be very great. A second reaction occurs between the red fumes and H_2O , which is injected in the form of steam, by which nitric acid and nitrogen dioxid are produced: $3\text{N}_2\text{O}_4 + 2\text{H}_2\text{O} = 4\text{HNO}_3 + 2\text{NO}$. The nitrogen dioxid in turn combines with O to produce the tetroxid, which then regenerates a further quantity of nitric acid, and so on. This series of reactions is made to go on continuously, the nitric acid being constantly regenerated, and acting merely as a carrier of O from the air to the SO_2 , in such manner that the sum of the reactions may be represented by the following equation: $2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{H}_2\text{SO}_4$.

The acid is allowed to collect in the chambers until it has the sp. gr. 1.55, when it is drawn off. This *chamber acid*, although used in a few industrial processes, is not yet strong enough for most purposes. It is concentrated, first, by evaporation in shallow leaden pans, until its sp. gr. reaches 1.746. At this point it begins to act upon the lead, and is transferred to platinum stills, where the concentration is completed.

Varieties.—Sulfuric acid is met with in several conditions of concentration and purity:

(1) The *commercial oil of vitriol*, largely used in manufacturing processes, is a more or less deeply colored, oily liquid, varying in sp. gr. from 1.833 to 1.842, and in concentration from 93 per cent to $99\frac{1}{2}$ per cent of true H_2SO_4 .

(2) *C. P. acid* = **Acidum sulfuricum** (U. S.; Br.), of sp. gr. 1.84, colorless and comparatively pure (see below).

(3) *Glacial sulfuric acid* is a hydrate of the composition H_2SO_4 , H_2O , sometimes called *bihydrated sulfuric acid*, which crystallizes in rhombic prisms, fusible at $+8.5^\circ$ (47.3° F.) when an acid of sp. gr. 1.788 is cooled to that temperature.

(4) *Ac. sulf. dil.* (U. S.; Br.) is a dilute acid of sp. gr. 1.069 and containing between 9 and 10 per cent. H_2SO_4 (U. S.), or of sp. gr. 1.094, containing between 12 and 13 per cent. H_2SO_4 (Br.).

Properties.—*Physical.*—A colorless, heavy, oily liquid; sp. gr. 1.842 at 12° (53.7° F.); crystallizes at 10.5° (50.9° F.); boils at 338° (640.4° F.). It is odorless, intensely acid in taste and reaction, and highly corrosive. It is non-volatile at ordinary temperatures. Mix-

tures of the acid with H_2O have a lower boiling point, and lower sp. gr. as the proportion of H_2O increases.

Chemical.—At a red heat vapor of H_2SO_4 is partly dissociated into SO_3 and H_2O ; or, in the presence of platinum, into SO_2 , H_2O and O . When heated with S , C , P , Hg , Cu , or Ag , it is reduced with formation of SO_2 .

Sulfuric acid has a great tendency to absorb H_2O , the union being attended with elevation of temperature, increase of bulk, and diminution of sp. gr. of the acid, and contraction of volume of the mixture. Three parts, by weight, of acid of sp. gr. 1.842, when mixed with one part of H_2O produce an elevation of temperature to 130° (266°F.), and the resulting mixture occupies a volume 1-6 less than the sum of the volumes of the constituents. Strong H_2SO_4 is a good desiccator of air or gases. It should not be left exposed in uncovered vessels, lest by increase of volume it overflow. When it is to be diluted with H_2O , the acid should be added to the H_2O in a vessel of thin glass, to avoid the projection of particles, or the rupture of the vessel. It is by virtue of its affinity for H_2O that H_2SO_4 chars or dehydrates organic substances. Sulfuric acid is a powerful dibasic acid.

The commercial acid is very impure. The colorless so-called C. P. acid may also contain: PbSO_4 , which forms a black ppt. when the dilute acid is treated with H_2S ; SO_2 , which gives off H_2S when the dilute acid is added to Zn ; As , which appears as a mirror when the dilute acid is examined by Marsh's test; oxids of nitrogen, which communicate a red or pink color to pure brucin.

Sulfates. Sulfuric acid being dibasic, there exist two sulfates of the univalent metals: HKSO_4 and K_2SO_4 , and but one sulfate of each bivalent metal: CaSO_4 . The sulfates of Ba , Ca , Sr , and Pb are insoluble, or very sparingly soluble, in H_2O . Other sulfates are soluble in H_2O , but all are insoluble in alcohol.

Analytical Characters.—Because of the dibasic character of sulfuric acid its solutions and those of its salts may contain two kinds of anion: SO_4'' in dilute solutions of the acid and in solutions of neutral sulfates, and $\text{SO}_4\text{H}'$ in concentrated solutions of the acid (p. 74) and in solutions of acid sulfates. In the following analytical reactions it is immaterial which anion is present if the reaction be only slightly acid, because then, as SO_4'' is removed by combination with the cations Ba'' , Pb'' , or Ca'' , the anion $\text{SO}_4\text{H}'$ is decomposed to $\text{SO}_4'' + \text{H}'$; but when the solution is strongly acid a small proportion of $\text{SO}_4\text{H}'$ may remain unprecipitated.

(1) Barium chlorid (or nitrate); a white ppt., insol. in dil. acids. The ppt., dried and heated with charcoal, forms BaS , which, with HCl , gives off H_2S . (2) Plumbic acetate forms a white ppt., insol. in dil.

acids. (3) Calcium chlorid forms a white ppt., either immediately or upon dilution with two volumes of alcohol: insol. in dil. HCl or HNO_3 .

Toxicology.—Sulfuric acid is an active corrosive, and may be, if taken in sufficient quantity in a highly diluted state, a true poison. The concentrated acid causes death, either within a few hours, by corrosion and perforation of the walls of the stomach and oesophagus, or, after many weeks, by starvation, due to destruction of the gastric mucous membrane and closure of the pyloric orifice of the stomach.

The treatment is the same as that for corrosion by HCl (see page 132).

Persulfuric Acid.— $\text{H}_2\text{S}_2\text{O}_8$ —194—is formed by the electrolysis of concentrated sulfuric acid: $2\text{H}_2\text{SO}_4 = \text{H}_2\text{S}_2\text{O}_8 + \text{H}_2$; or by the action of hydrogen peroxid on sulfuric acid: $2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 = \text{H}_2\text{S}_2\text{O}_8 + 2\text{H}_2\text{O}$. It crystallizes at 0° in long, transparent needles. The corresponding anhydrid, S_2O_7 , is formed by the action of high tension electric currents in a mixture of dry SO_2 and O.

Thiosulfuric Acid.—*Hyposulfurous acid*— $\text{H}_2\text{S}_2\text{O}_3$ —114—may be considered as sulfuric acid, H_2SO_4 , in which one atom of oxygen has been replaced by one of sulfur. The acid itself has not been isolated, being decomposed, on liberation from the thiosulfates, into sulfur, water, and sulfur dioxide: $\text{H}_2\text{S}_2\text{O}_3 = \text{S} + \text{SO}_2 + \text{H}_2\text{O}$.

Pyrosulfuric Acid.—*Fuming sulfuric acid*—*Nordhausen oil of vitriol*—*Disulfuric hydrate*— $\text{H}_2\text{S}_2\text{O}_7$ —*Molecular weight*=178—*Sp. gr.*=1.9—*Boils at* 52.2° (126°F).

Preparation.—By distilling ferrous sulfate; and purification of the product by repeated crystallizations and fusions, until a substance fusing at 35° (95°F .) is obtained.

Properties.—The commercial Nordhausen acid, which is a mixture of $\text{H}_2\text{S}_2\text{O}_7$ with excess of SO_3 , or of H_2SO_4 , is a brown, oily liquid, which boils below 100° (212°F .) giving off SO_3 ; and is solid or liquid according to the temperature. It is used chiefly as a solvent for indigo, and in the anilin industry.

SELENIUM AND TELLURIUM.

Se—78.5 Te—126.

These are rare elements which form compounds similar to those of sulfur. Elementary selenium is used in some forms of electrical apparatus.

III. NITROGEN GROUP.

NITROGEN—PHOSPHORUS—ARSENIC—ANTIMONY.

The elements of this group are trivalent or quinquivalent, occasionally univalent. With hydrogen they form non-acid compounds, composed of one volume of the element in the gaseous state with three volumes of hydrogen, the union being attended with a condensation of volume of one-half.

Bismuth, frequently classed in this group, is excluded, owing to the existence of the nitrate $\text{Bi}(\text{NO}_3)_3$. The relations existing between the compounds of the elements of this group are shown in the following table:

NH_3 ,	N_2O ,	NO ,	N_2O_3 ,	NO_2 ,	N_2O_5 ,	—
PH_3 ,	—	—	P_2O_3 ,	—	P_2O_5 ,	H_3PO_2 ,
AsH_3 ,	—	—	As_2O_3 ,	—	As_2O_5 ,	—
SbH_3 ,	—	—	Sb_2O_3 ,	Sb_2O_4	Sb_2O_5 ,	—
Hyd- rid.	Mon- oxid.	Di- oxid.	Tri- oxid.	Tetr- oxid.	Pent- oxid.	Hypo-ous acid.
—	—	HNO_2 ,	—	—	—	HNO_3 ,
H_3PO_3 ,	$\text{H}_4\text{P}_2\text{O}_5$,	—	H_3PO_4 ,	$\text{H}_4\text{P}_2\text{O}_7$,	HPO_3 ,	
H_3AsO_3 ,	$\text{H}_4\text{As}_2\text{O}_5$,	HAsO_2 ,	H_3AsO_4 ,	$\text{H}_4\text{As}_2\text{O}_7$,	HAsO_3 ,	
—	—	HSbO_2 ,	H_3SbO_4 ,	$\text{H}_4\text{Sb}_2\text{O}_7$,	HSbO_3 ,	
-ous acid.	Pyro-ous acid.	Meta-ous acid.	-ic acid.	Pyro-ic acid.	Meta-ic acid.	

While the hydrogen compounds of the halogens are strong acids, and those of the sulfur group are weak acids, NH_3 is strongly basic (see hydrazin, hydroxylamin and hydrazoic acid, pp. 151, 152), PH_3 is weakly basic, and AsH_3 and SbH_3 are neutral. Oxids of the types N_2O , NO and NO_2 are neutral, those of the types N_2O_3 and N_2O_5 are anhydrids. The oxyacids vary in basicity: the types H_3PO_2 , HNO_2 and HNO_3 are monobasic, H_3PO_3 dibasic, H_3PO_4 tribasic, and $\text{H}_4\text{P}_2\text{O}_5$ and $\text{H}_4\text{P}_2\text{O}_7$ tetrabasic.

NITROGEN.

Azote—*Symbol*=N—*Atomic weight*=14 (O=16:14.04; H=1: 13.93)—*Molecular weight*=28—*Sp. gr.*=0.9701—*One litre weighs* 1.254 grams—*Name from* νίτρον=nitre, γένεσις=source; or from ἀ, privative ζωή=life—*Discovered by* Mayow in 1669.

Occurrence.—Free in atmospheric air and in volcanic gases. In combination in the nitrates, in ammoniacal compounds and in a great number of animal and vegetable substances.

Preparation.—(1) By removal of O from atmospheric air; by burning P in air, or by passing air slowly over red-hot copper. It is contaminated with CO_2 , H_2O , etc.

(2) By passing Cl through excess of ammonium hydroxid solution. If ammonia be not maintained in excess, the Cl reacts with the ammonium chlorid formed, to produce the explosive nitrogen chlorid.

(3) By heating ammonium nitrite (NH_4NO_2): or a mixture of ammonium chlorid and potassium nitrite.

Properties.—A colorless, odorless, tasteless, non-combustible gas; not a supporter of combustion; very sparingly soluble in water.

It is very slow to enter into combination, and most of its compounds are very prone to decomposition, which may occur explosively or slowly. Nitrogen combines directly with O under the influence of electric discharges; and with H under like conditions, and, directly, during the decomposition of nitrogenized organic substances. It combines directly with magnesium, boron, vanadium, and titanium.

Nitrogen is not poisonous, but is incapable of supporting respiration.

Atmospheric Air.—The alchemists considered air as an element, until Mayow, in 1669, demonstrated its complex nature. It was not, however, until 1770 that Priestley repeated the work of Mayow; and that the compound nature of air, and the characters of its constituents were made generally known by the labors (1770–1781) of Priestley, Rutherford, Lavoisier, and Cavendish. The older chemists used the terms *gas* and *air* as synonymous.

Composition.—Air is not a chemical compound, but a mechanical mixture of O and N, with smaller quantities of other gases. Leaving out of consideration vapor of water and small quantities of other gases, except 0.03 of carbon dioxid, air consists of 20.95 O and 79.02 N (including argon), by volume; or about 23 O and 77 N, by weight; proportions which vary but very slightly at different times and places; the extremes of the proportion of O found having been 20.908 and 20.999.

That air is not a compound is shown by the fact that the proportion of its constituents does not represent a relation between their atomic weights, or between any multiples thereof; as well as by the solubility of air in water. Were it a compound it would have a definite degree of solubility of its own, and the dissolved gas would have the same composition as when free. But each of its constituents dissolves in H_2O according to its own solubility, and air dissolved in H_2O at 14.1° (57.4°F.) consists of N and O, not in the proportion given above, but in the proportion of 66.76 to 33.24.

Besides these two main constituents, air contains about thousandths of its bulk of other substances; vapor of water, carbon dioxide, ammoniacal compounds, hydrocarbons, ozone, oxides of nitrogen, and solid particles held in suspension.

Vapor of Water.—Atmospheric moisture is either visible, as fogs and clouds, when it is in the form of a finely divided liquid; invisible, as vapor of water. The amount of H_2O which a given volume of air can hold, without precipitation, varies according to temperature and the pressure. It happens rarely that air is as highly charged with moisture as it is capable of being for the existing temperature. The **fraction of saturation**, or **hygrometric state**, or **relative humidity** of the atmosphere is the percentage of that quantity of vapor of water which the air could hold at the existing temperature and pressure which it actually does hold. Thus air with a humidity of 100 is saturated, and a diminution of temperature or of pressure would cause precipitation; but an increase of temperature or of pressure would cause a diminution of humidity. Ordinarily air contains from 66 to 70 per cent. of its possible amount of moisture. If the quantity be less than this, the air is dry, and causes a parched sensation, and the sense of "stuffiness" so common in furnace-heated houses. If it be greater, evaporation from the skin is impeded, the air is oppressive if warm.

The actual amount of moisture in air is determined by passing a known volume through tubes filled with calcium chloride; the increase in weight represents the amount of H_2O in the volume of air used. The humidity is determined by instruments called **hygrometers**, **hygroscopes** or **psychrometers**.

Carbon Dioxid.—The quantity of carbon dioxide in free air varies from 3 to 6 parts in 10,000 by volume. (See Carbon dioxide.)

Ammoniacal Compounds.—Carbonate, nitrate, and nitrite of ammonium occur in small quantity (0.1 to 6.0 parts per million of NH_3) in air, as products of the decomposition of nitrogenized organic substances. They are absorbed and assimilated by plants.

Nitric and Nitrous acids, usually in combination with ammonium, are produced either by the oxidation of combustible substances containing N, or by direct union of N and H_2O during discharge of atmospheric electricity. Rain-water, falling during thunder-showers, has been found to contain as much as 3.71 per million of HNO_3 .

Sulfuric and Sulfurous acids occur, in combination with ammonium, in the air over cities, and manufacturing districts, where they are produced by the oxidation of S, existing in coal and coal-gas.

Solid particles of the most diverse nature are always present in the air and become visible in a beam of sunlight. Sodium chloride is almost always present, always in the neighborhood of salt water.

Air contains myriads of germs of vegetable organisms, mould, etc., which are propagated by the transportation of these germs by air-currents.

Compounds of Nitrogen and Hydrogen.—Three are known: **Ammonia**, NH_3 ; **Hydrazin**, N_2H_4 ; and **Hydrazoic acid**, N_3H ; as well as salts corresponding to two hydroxids.

Ammonia.—*Hydrogen nitrid*—*Volatile alkali*— NH_3 —*Molecular weight*=17—*Sp. gr.*=0.589 *A*—*Liquefies at* -40° (-40° F.)—*Boils at* -33.7° (-28.7° F.)—*Solidifies at* -75° (-103° F.)—*A litre weighs* 0.7655 gram.

Preparation.—(1) By union of nascent H with N.

(2) By decomposition of organic matter containing N, either spontaneously or by destructive distillation.

(3) By heating solution of ammonium hydroxid: $\text{NH}_4\text{HO}=\text{NH}_3+\text{H}_2\text{O}$.

Properties.—*Physical.*—A colorless gas, having a pungent odor, and an acrid taste. It is very soluble in H_2O , 1 volume of which at 0° (32° F.) dissolves 1050 vols. NH_3 , and at 15° (59° F.), 727 vols. NH_3 . Alcohol and ether also dissolve it readily. Liquid ammonia is a colorless, mobile fluid, used in ice machines for producing artificial cold, the liquid absorbing a great amount of heat in volatilizing.

Chemical.—At a red heat ammonia is decomposed into a mixture of N and H, occupying double the volume of the original gas. It is similarly decomposed by the prolonged passage through it of discharges of electricity. It is not readily combustible, yet it burns in an atmosphere of O with a yellowish flame. Mixtures of NH_3 with O, nitrogen monoxid, or nitrogen dioxid, explode on contact with flame.

The solution of ammonia in H_2O constitutes a strongly alkaline liquid, known as **aqua ammoniæ**, which is possessed of strongly basic properties. It is neutralized by acids with the formation of crystalline salts, which are also formed, without liberation of hydrogen, by direct union of gaseous NH_3 with acid vapors. The ammoniacal salts and the alkaline base in aqua ammoniæ are compounds of a radical, **ammonium**, NH_4 , which forms compounds corresponding to those of potassium or sodium. The compound formed by the union of ammonia and water is **ammonium hydroxid**, NH_4HO : $\text{NH}_3+\text{H}_2\text{O}=\text{NH}_4\text{HO}$; and that formed by the union of hydrochloric acid and ammonia is **ammonium chlorid**, NH_4Cl : $\text{NH}_3+\text{HCl}=\text{NH}_4\text{Cl}$.

A very delicate test for ammonia is Nessler's reagent. This is made by dissolving 35 gm. of potassium iodid and 13 gm. of mercuric chlorid in 800 cc. H_2O . A cold, saturated solution of mercuric chlorid is then added, drop by drop, until the red precipitate formed no longer redissolves on agitation; 160 gm. of potassium hydroxid

are then dissolved in the liquid, which is finally made up to 1000 cc. It gives a yellow color with a mere trace of NH_3 , and a red-brown precipitate with a larger amount.

Hydrazin—Diamid— $\text{H}_2\text{N.NH}_2$ —is obtained by heating its hydroxid with anhydrous BaO , or by decomposing its chlorhydrate with sodium methylate. It is a liquid, b. p. 113.5° , which does not attack glass, sp. gr. 1.014. Mixes with water and with alcohols. It is quite stable, and only decomposes at 350° : $3\text{N}_2\text{H}_4 = \text{N}_2 + 4\text{NH}_3$. It is a powerful reducing agent, and reacts violently with easily reducible oxids and with oxidizing agents. It ignites in chlorin, and burns in air with a blue flame. It forms a hydroxid and salts, corresponding to those of ammonium, in which one N atom is quinquivalent: $\text{H}_2\text{N.NH}_3\text{OH}$. The hydroxid is obtained by distilling the sulfate with KHO in an apparatus entirely of silver. It is a colorless liquid which when cold attacks cork and rubber, and glass when heated. It mixes with water or alcohol in all proportions, but not with ether. It is an extremely powerful reducing agent: $\text{H}_2\text{N.NH}_3\text{OH} + \text{O}_2 = \text{N}_2 + 3\text{H}_2\text{O}$, and explodes with easily reducible oxids. The sulfate, from which the hydrate is obtained, is formed in several reactions, mostly with organic compounds, as from triazoaetic acid, and from guanidin (q. v.). It is an active poison.

Hydrazoic Acid—Azoimid— N_3H —is a substance recently obtained from benzoyl-azoimid, which, although containing the same elements as ammonia, is distinctly acid in character. It is a colorless liquid, boiling at 37° (98.6°F.), having a very pungent and unpleasant odor. It is extremely unstable and explodes with great violence. It reacts with metals, oxids, and hydroxids, as does hydrochloric acid, to form nitrids, which, like the free acid, are very explosive. It is a very active poison.

Hydroxylamin— NH_2HO —33.—The amins and amids (q. v.) are compounds derived from ammonia by the substitution of radicals for a part or all of its hydrogen. This substance, which is intermediate in composition between ammonia and ammonium hydroxid, may be considered as ammonia, one of whose hydrogen atoms has been replaced by the radical hydroxyl, HO . It is obtained in aqueous solution by the union of nascent hydrogen with nitrogen dioxid: $\text{NO} + \text{H}_2 = \text{NH}_2\text{HO}$; or by the action of nascent hydrogen upon nitric acid: $\text{HNO}_3 + 3\text{H}_2 = 2\text{H}_2\text{O} + \text{NH}_2\text{HO}$. Hydroxylamin has been obtained in colorless, hygroscopic crystals, fusing at 33° (91.4°F.), by systematic rectification of the methyl alcohol solution under diminished pressure, and by distillation of the Zn double salt, $\text{ZnCl}_2, 2\text{NH}_2\text{OH}$ with anilin. Its aqueous solution, which probably contains the corresponding hydroxid, NH_3O , HO , is strongly alkaline and behaves with regard to acids as does ammonium hydroxid solution, forming salts corresponding to those of ammonium. Thus hydroxyl-ammo-

nium chlorid, NH_4OCl , crystallizes in prisms or tables, fusible at 100° (212°F.), and decomposed into HCl , H_2O and NH_4Cl at a slightly higher temperature. It is a very powerful reducing agent.

Hydroxylammonium chlorid has been used in the treatment of cutaneous disorders. It is an actively toxic agent, converting oxy-hæmoglobin into methæmoglobin.

Compounds of Nitrogen with the Halogens.—**Nitrogen Chlorid**— NCl_3 —120.5—is formed by the action of excess of Cl upon NH_3 or an ammoniacal compound. It is an oily, light-yellow liquid; sp. gr. 1.653; has been distilled at 71° (159.8F.). When heated to 96° (204.8°F.), when subjected to concussion, or when brought in contact with phosphorus, alkalies or greasy matters, it is decomposed, with a violent explosion, into one volume N and three volumes Cl .

Nitrogen Bromid.— NBr_3 —254—has been obtained as a reddish-brown, syrupy liquid, very volatile, and resembling the chlorid in its properties, by the action of potassium bromid upon nitrogen chlorid.

Nitrogen Iodid.— NI_3 —395—When iodine is brought in contact with ammonium hydroxid solution, a dark brown or black powder, highly explosive when dried, is formed. This substance varies in composition according to the conditions under which the action occurs; sometimes the iodid alone is formed; under other circumstances it is mixed with compounds containing N , I , and H .

Oxids of Nitrogen.—Five are known, forming a regular series: N_2O , NO , N_2O_3 , N_2O_4 , N_2O_5 . Of these two, the trioxid, N_2O_3 , and pentoxid, N_2O_5 , are anhydrids.

Nitrogen Monoxid.—*Nitrous oxid—Laughing gas—Nitrogen protoxid*— N_2O —*Molecular weight*=44—*Sp. gr.*=1.527 *A*—*Fuses at* -100° (-148°F.)—*Boils at* -87° (-124°F.)—*Discovered in 1776 by Priestley.*

Preparation.—By heating ammonium nitrate: $(\text{NH}_4)\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. To obtain a pure product there should be no ammonium chlorid present (as an impurity of the nitrate), and the heat should be applied gradually, and not allowed to exceed 250° (482°F.), and the gas formed should be passed through wash-bottles containing sodium hydroxid and ferrous sulfate.

Properties.—*Physical.*—A colorless, odorless gas, having a sweetish taste; soluble in H_2O ; more so in alcohol. Under a pressure of 30 atmospheres, at 0° (32°F.), it forms a colorless, mobile liquid which, when dissolved in carbon disulfid and evaporated *in vacuo*, produces a cold of -140° (-220°F.).

Chemical.—It is decomposed by a red heat and by the continuous passage of electric sparks. It is not combustible, but is, after oxygen, the best supporter of combustion known.

Physiological.—Although, owing to the readiness with which N_2O is decomposed into its constituent elements, and the nature and relative proportions of these elements, it is capable of maintaining respiration longer than any gas except oxygen or air, an animal will live for a short time only in an atmosphere of pure nitrous oxid. When inhaled, diluted with air, it produces the effects first observed by Davy in 1799: first an exhilaration of spirits, frequently accompanied by laughter, and a tendency to muscular activity, the patient sometimes becoming aggressive; afterward there is complete anæsthesia and loss of consciousness. It has been much used, by dentists especially, as an anæsthetic in operations of short duration, and in one or two instances anæsthesia has been maintained by its use for nearly an hour.

A solution in water under pressure, containing five volumes of the gas, is sometimes used for internal administration.

Nitrogen Dioxid.—*Nitric oxid*— NO —*Molecular weight*=30—*Sp. gr.*=1.039 *A*—*Discovered by Hales in 1772.*

Preparation.—By the action of copper on moderately diluted nitric acid in the cold: $3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu}(\text{NO}_3)_2 + 4\text{H}_2\text{O} + 2\text{NO}$; the gas being collected after displacement of air from the apparatus.

Properties.—A colorless gas, whose odor and taste are unknown; very sparingly soluble in H_2O ; more soluble in alcohol. The sp. gr. of the gas has been determined at -100° (-148°F.) and has been found to be same as at the ordinary temperature. This fixes the molecular weight at 30 and gives the formula NO , which is difficult to reconcile with the theory of valence. Were the formula doubled the constitution of this gas could be thus expressed: $\text{O}=\text{N}-\text{N}=\text{O}$. (See Nitrogen tetroxid.)

It combines with O, when mixed with that gas or with air, to form the reddish brown nitrogen tetroxid. It is absorbed by solution of ferrous sulfate, to which it communicates a dark brown or black color. It is neither combustible nor a good supporter of combustion, although ignited C and P continue to burn in it, and the alkaline metals, when heated in it, combine with its O with incandescence.

Nitrogen Trioxid.—*Nitrous anhydrid*— N_2O_3 —76—Is prepared by the direct union of nitrogen dioxid and oxygen at low temperatures, or by decomposing liquefied nitrogen tetroxid with a small quantity of H_2O at a low temperature: $4\text{NO}_2 + \text{H}_2\text{O} = 2\text{HNO}_3 + \text{N}_2\text{O}_3$. It is a dark indigo-blue liquid, which, boiling at about 0° (32°F.), is partly decomposed. It solidifies at -82° (-115.6°F.).

Nitrogen Tetroxid.—*Nitrogen peroxid—Hyponitric acid—Nitrous fumes*— N_2O_4 —*Molecular weight*=92—*Boils at* 22° (71.6° F.)—*Solidifies at* 9° (15.8° F.).

Preparation.—(1) By mixing one volume O with two volumes NO; both dry and ice-cold.

(2) By heating perfectly dry lead nitrate, O being also produced:
 $2\text{Pb}(\text{NO}_3)_2 = 2\text{PbO} + 4\text{NO}_2 + \text{O}_2$.

(3) By dropping strong nitric acid upon a red-hot platinum surface.

Properties.—When pure and dry, it is an orange-yellow liquid at the ordinary temperature; the color being darker the higher the temperature; the gas is red-brown, but becomes colorless at about 500° (932° F.). The red fumes, which are produced when nitric acid is decomposed by starch or by a metal, consist of N_2O_4 , mixed with N_2O_3 . The sp. gr. of the gas varies with the temperature and pressure. Values varying from 29.23 to 39.9 have been obtained ($\text{H}=1$). The molecular formula, NO_2 , calls for sp. gr. 23; N_2O_4 for 46. These variations are due to the fact that the gas is dissociated (p. 90) at comparatively low temperatures. The formula N_2O_4 has been fixed as the correct one by the method of Raoult (see p. 68). It dissolves in nitric acid, forming a dark yellow liquid, which is blue or green if N_2O_3 be also present. With SO_2 it combines to form a solid, crystalline compound, which is sometimes produced in the manufacture of H_2SO_4 . This substance, which forms the **lead chamber crystals**, is a substituted sulfurous acid, **nitrosulfonic acid**, $\text{NO}_2\text{SO}_2\text{OH}$ (see sulfonic acids). A small quantity of H_2O decomposes N_2O_4 into HNO_3 and N_2O_3 , which latter colors it green or blue. A larger quantity of H_2O decomposes it into HNO_3 and NO. By bases it is transformed into a mixture of nitrite and nitrate:
 $2\text{NO}_2 + 2\text{KHO} = \text{KNO}_2 + \text{KNO}_3 + \text{H}_2\text{O}$.

It is an energetic oxydant, for which it is largely used. With certain organic substances it does not behave as an oxydant, but becomes substituted as an univalent radical; thus with benzene it forms nitro-benzene: $\text{C}_6\text{H}_5(\text{NO}_2)$.

Toxicology.—The brown fumes given off during many processes, in which nitric acid is decomposed, are dangerous to life. All such operations, when carried on on a small scale, as in the laboratory, should be conducted under a hood or some other arrangement, by which the fumes are carried into the open air. When in industrial processes the volume of gas formed becomes such as to be a nuisance when discharged into the air, it should be utilized in the manufacture of H_2SO_4 , or absorbed by H_2O or an alkaline solution.

An atmosphere contaminated with brown fumes is more dangerous

than one containing Cl, as the presence of the latter is more immediately annoying. At first there is only coughing, and it is only two to four hours later that a difficulty in breathing is felt, death occurring in ten to fifteen hours. At the autopsy the lungs are found to be extensively disorganized and filled with black fluid.

Even air containing small quantities of brown fumes, if breathed for a long time, produces chronic disease of the respiratory organs. To prevent such accidents, thorough ventilation in locations where brown fumes are liable to be formed is imperative. In cases of spilling nitric acid, safety is to be sought in retreat from the apartment until the fumes have been replaced by pure air from without.

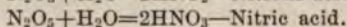
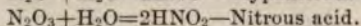
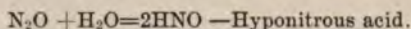
Nitrogen Pentoxid.—*Nitric anhydrid*— N_2O_5 —*Molecular weight* = 108—*Fuses at* 30° (86° F.)—*Boils at* 47° (116.6° F.).

Preparation.—(1) By decomposing dry silver nitrate with dry Cl in an apparatus entirely of glass: $4\text{AgNO}_3 + 2\text{Cl}_2 = 4\text{AgCl} + 2\text{N}_2\text{O}_5 + \text{O}_2$.

(2) By removing water from fuming nitric acid with phosphorus pentoxid: $6\text{HNO}_3 + \text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4 + 3\text{N}_2\text{O}_5$.

Properties.—Prismatic crystals at temperatures above 30° (86° F.). It is very unstable, being decomposed by a heat of 50° (122° F.); on contact with H_2O , with which it forms nitric acid; and even spontaneously. Most substances which combine readily with O remove that element from N_2O_5 .

Nitrogen Acids.—Three are known, either free or in combination, corresponding to the three oxids containing uneven numbers of O atoms:



Hyponitrous Acid— HNO —31—Known only in combination. Sodium hyponitrite is formed by the action of sodium upon sodium nitrate, or nitrite: $\text{NaNO}_3 + 4\text{Na} + 2\text{H}_2\text{O} = \text{NaNO} + 4\text{NaHO}$. Silver hyponitrite is formed by reduction of sodium nitrate by nascent H and decomposition with silver nitrate.

Nitrous Acid—*Metanitrous acid*— HNO_2 —47—has not been isolated, although its salts, the nitrites, are well-defined compounds: $\text{M}'\text{NO}_2$ or $\text{M}''(\text{NO}_2)_2$.

The *nitrites* occur in nature, in small quantity, in natural waters, where they result from the decomposition of nitrogenous organic substances; also in saliva. They are produced by heating the corresponding nitrate, either alone or in the presence of a readily oxidizable metal, such as lead. Solutions of the nitrites are readily decomposed

by the mineral acids, with evolution of brown fumes. They take up oxygen readily and are hence used as reducing agents. Solutions of potassium permanganate are instantly decolorized by nitrites. A mixture of thin starch paste and zinc iodid solution is colored blue by nitrites, which decompose the iodid, liberating the iodine. A solution of metaphenylenediamine, in the presence of free acid, is colored brown by very minute traces of a nitrite, the color being due to the formation of triamido-azobenzene (Bismark brown).

Nitric Acid. Aquafortis—Hydrogen nitrate—Acidum nitricum—U. S.; Br.— HNO_3 —63.

Preparation.—(1) By the direct union of its constituent elements under the influence of electric discharges.

(2) By the decomposition of an alkaline nitrate by strong H_2SO_4 . With moderate heat a portion of the acid is liberated. $2\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{NaNO}_3 + \text{HNO}_3$, and at a higher temperature the remainder is given off: $\text{NaNO}_3 + \text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{HNO}_3$. This is the reaction used in the manufacture of HNO_3 .

Varieties.—**Commercial**—a yellowish liquid, impure, and of two degrees of concentration: **single aquafortis**; sp. gr. about 1.25=39% HNO_3 ; and **double aquafortis**; sp. gr. about 1.4=64% HNO_3 . **Fuming**—a reddish yellow liquid, more or less free from impurities; charged with oxids of nitrogen. Sp. gr. about 1.5. Used as an oxidizing agent. **C. P.**—a colorless liquid, sp. gr. 1.522, which should respond favorably to the tests given below. **Acidum nitricum**, U. S.; Br.—a colorless acid, of sp. gr. 1.42=70% HNO_3 . **Acidum nitricum dilutum**, U. S.; Br.—the last mentioned, diluted with H_2O to sp. gr. 1.059=10% HNO_3 (U. S.), or to sp. gr. 1.101=17.44% HNO_3 (Br.).

Properties.—**Physical.**—The pure acid is a colorless liquid: sp. gr. 1.522; boils at 86° (186.8° F.); solidifies at -40° (-40° F.); gives off white fumes in damp air; and has a strong acid taste and reaction. The sp. gr. and boiling point of dilute acids vary with the concentration. If a strong acid be distilled, the boiling-point gradually rises from 86° (186.8° F.) until it reaches 123° (253.4° F.), when it remains constant, the sp. gr. of distilled and distillate being 1.42=70% HNO_3 . If a weak acid be taken originally the boiling point rises until it becomes stationary at the same point.

Chemical.—When exposed to air and light, or when strongly heated, HNO_3 is decomposed into N_2O_4 , H_2O and O. Nitric acid is a valuable oxydant; it converts I, P, S, C, B, and Si or their lower oxids into their highest oxids; it oxidizes and destroys most organic substances, although with some it forms products of substitution. Most of the metals dissolve in HNO_3 as nitrates, a portion of the

acid being at the same time decomposed into NO and H_2O : $4HNO_3 + 3Ag = 3AgNO_3 + NO + 2H_2O$. The chemical activity of HNO_3 is much reduced, or even almost arrested, when the intervention of nitrous acid is prevented by the presence of carbamid. The so-called "noble metals," gold and platinum, are not dissolved by either HNO_3 or HCl , but dissolve as chlorids in a mixture of the two acids, called **aqua regia**. In this mixture the two acids mutually decompose each other according to the equations: $HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$ and $2HNO_3 + 6HCl = 4H_2O + 2NOCl_2 + Cl_2$ with formation of **nitrosyl chlorid**, $NOCl$ and **bichlorid**, $NOCl_2$, and nascent Cl ; the last named combining with the metal. Iron dissolves easily in dilute HNO_3 , but if dipped into the concentrated acid, it is rendered **passive**, and does not dissolve when subsequently brought in contact with the dilute acid. This passive condition is destroyed by a temperature of 40° ($104^\circ F.$) or by contact with Pt, Ag or Cu. When HNO_3 is decomposed by zinc or iron, or in the porous cup of a Grove battery, N_2O_3 and N_2O_4 are formed, and dissolve in the acid, which is colored dark yellow, blue or green. An acid so charged is known as **nitroso-nitric acid**. Nitric acid is monobasic.

Impurities.—Oxids of nitrogen color the acid yellow: H_2SO_4 gives a white ppt. with $BaCl_2$; Cl , a white ppt. with $AgNO_3$; and Fe a red color with ammonium thiocyanate. Dilute the acid with two volumes of water before testing. Salts leave a solid residue when the acid is evaporated in platinum.

Nitrates.—The nitrates of K and Na occur in nature. Nitrates are formed by the action of HNO_3 on the metals, or on their oxids or carbonates. They have the composition $M'NO_3$, $M''(NO_3)_2$ or $M'''(NO_3)_3$, except certain basic salts, such as the sesquibasic lead-nitrate, $Pb(NO_3)_2 \cdot 2PbO$. With the exception of a few basic salts, the nitrates are all soluble in water. When heated, they fuse and act as powerful oxidants. They are decomposed by H_2SO_4 with liberation of HNO_3 .

Analytical Characters.—As the nitrates are all soluble, there is no precipitation reaction for the anion NO_3' , and recourse is had to color reactions: (1) Add an equal volume of concentrated H_2SO_4 , cool, and float on the surface of the mixture a solution of $FeSO_4$. The lower layer becomes gradually colored brown, black, or purple, beginning at the top.

(2) Boil in a test-tube a small quantity of HCl , containing enough sulfindigotic acid to communicate a blue color, add the suspected solution and boil again; the color is discharged.

(3) If acid, neutralize with KHO , evaporate to dryness, add to the residue a few drops of H_2SO_4 and a crystal of brucin (or some sulfanilic acid); a red color is produced.

(4) Add H_2SO_4 and Cu to the suspected liquid and boil, brown fumes appear (best visible by looking into the mouth of the test tube).

(5) A solution of diphenylamin in concentrated H_2SO_4 (.01 grm. in 100 cc.) is colored blue by nitric acid. A similar color is produced by other oxidizing agents.

(6) To 0.5 cc. nitrate solution add one drop aqueous solution of resorcinol (10%), and 1 drop HCl (15%), and float on the surface of 2 cc. concentrated H_2SO_4 ; a purple-red band.

Toxicology.—Although most of the nitrates are poisonous when taken internally in sufficiently large doses, their action seems to be due rather to the metal than to the acid radical. Nitric acid itself is one of the most powerful of corrosives.

Any animal tissue with which the concentrated acid comes in contact is rapidly disintegrated. A yellow stain, afterward turning to dirty brownish, or, if the action be prolonged, an eschar, is formed. When taken internally, its action is the same as upon the skin, but owing to the more immediately important function of the parts, is followed by more serious results (unless a large cutaneous surface be destroyed).

The symptoms following its ingestion are the same as those produced by the other mineral acids, except that all parts with which the acid has come in contact, including vomited shreds of mucous membrane, are colored yellow. The treatment is the same as that indicated when H_2SO_4 or HCl have been taken, i. e., neutralization of the corrosive by magnesia or soap, and dilution.

PHOSPHORUS.

Symbol—P—*Atomic weight*—31 (O=16:31; H=1:30.74)—*Molecular weight*—124 (P_4)—*Sp. gr. of vapor*—4.2904 *A*—*Name from φῶς* =light, φέρω=I bear—*Discovered by Brandt in 1669*—Phosphorus (U. S.; Br.).

Occurrence.—Only in combination; in the mineral and vegetable worlds as phosphates of Ca, Mg, Al, Pb, K, Na. In the animal kingdom as phosphates of Ca, Mg, K and Na, and in organic combination.

Preparation.—From bone-ash, in which it occurs as tricalcic phosphate. Three parts of bone-ash are digested with 2 parts of strong H_2SO_4 , diluted with 20 volumes H_2O , when insoluble calcic sulfate and the soluble monocalcic phosphate, or "superphosphate," are formed: $\text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{SO}_4 = \text{H}_4\text{Ca}(\text{PO}_4)_2 + 2\text{CaSO}_4$. The solution of superphosphate is filtered off and evaporated, the residue is mixed with about one-fourth its weight of powdered charcoal and

sand, and the mixture heated, first to redness, finally to a white heat, in earthenware retorts, whose beaks dip under water in suitable receivers. During the first part of the heating the monocalcic phosphate is converted into metaphosphate: $\text{CaH}_4(\text{PO}_4)_2 = \text{Ca}(\text{PO}_3)_2 + 2\text{H}_2\text{O}$; which is in turn reduced by the charcoal, with formation of carbon monoxid and liberation of phosphorus, while the calcium is combined as silicate: $2\text{Ca}(\text{PO}_3)_2 + 2\text{SiO}_2 + 5\text{C} = 2\text{CaSiO}_3 + 10\text{CO} + \text{P}_4$.

A direct electric process has, in great part, replaced the above industrially. A mixture of phosphate, carbon and flux is heated in a closed electric furnace provided with a condenser. The process is continuous and avoids the use of H_2SO_4 .

The crude product is purified by fusion, first under a solution of bleaching powder, next under ammoniacal H_2O , and finally under water containing a small quantity of H_2SO_4 and potassium dichromate. It is then strained through leather and cast into sticks under warm H_2O .

Properties.—Physical.—Phosphorus is capable of existing in four allotropic forms:

(1) *Ordinary, or yellow variety*, in which it usually occurs in commerce. This is a yellowish, translucent solid, of the consistency of wax. Below 0° (32°F.) it is brittle; it fuses at 44.3° (111.7°F.); and boils at 290° (554°F.) in an atmosphere not capable of acting upon it chemically. Its vapor is colorless; sp. gr. = 4.5A—65 H at 1040° (1940°F.). It volatilizes below its boiling point, and H_2O boiled upon it gives off steam charged with its vapor. Exposed to air it gives off white fumes and produces ozone. It is luminous in the dark. It is insoluble in H_2O ; sparingly soluble in alcohol, more soluble in ether; soluble in carbon disulfid, and in the fixed and volatile oils. It crystallizes on evaporation of its solutions in octahedra or dodecahedra. Sp. gr. 1.83 at 10° (50°F.).

(2) *White phosphorus* is formed as a white, opaque pellicle upon the surface of the ordinary variety, when this is exposed to light under aerated H_2O . Sp. gr. 1.515 at 15° (59°F.). When fused it reproduces ordinary phosphorus without loss of weight.

(3) *Black variety* is formed when ordinary phosphorus is heated to 70° (158°F.) and suddenly cooled.

(4) *Red variety* is produced from the ordinary by maintaining it at from 240° (464°F.) to 280° (536°F.) for two or three days, in an atmosphere of carbon dioxid; and, after cooling, washing out the unaltered yellow phosphorus with carbon disulfid. It is also formed upon the surface of the yellow variety, when it is exposed to direct sunlight.

It is a reddish, odorless, tasteless solid, which does not fume in air, nor dissolve in the solvents of the yellow variety. Sp. gr. 2.1.

Heated to 500° (932° F.) with lead, in the absence of air, it dissolves in the molten metal, from which it separates on cooling in violet-black, rhombohedral crystals, of sp. gr. 2.34. If prepared at 250° (482° F.) it fuses below that temperature, and at 260° (500° F.) is transformed into the yellow variety, which distils. The crystalline product does not fuse. It is not luminous at ordinary temperatures.

Chemical.—The most prominent property of P is the readiness with which it combines with O. The yellow variety ignites and burns with a bright flame if heated in air to 60° (140° F.), or if exposed in a finely-divided state to air at the ordinary temperature; with formation of P_2O_3 ; P_2O_5 ; H_3PO_3 , or H_3PO_4 , according as O is present in excess or not, and according as the air is dry or moist. The temperature of ignition of yellow P is so low that it must be preserved under boiled water. By directing a current of O upon it, P may be burned under H_2O , heated above 45° (113° F.). The red variety combines with O much less readily, and may be kept in contact with air without danger.

The luminous appearance of yellow P is said to be due to the formation of ozone. It does not occur in pure O at the ordinary temperature, nor in air under pressure, nor in the absence of moisture, nor in the presence of minute quantities of carbon disulfid, oil of turpentine, alcohol, ether, naphtha, and many gases.

Yellow phosphorus burns in Cl with formation of PCl_3 or PCl_5 , according as P or Cl is present in excess. Both yellow and red varieties combine directly with Cl, Br, and I.

Phosphorus is not acted on by HCl or cold H_2SO_4 . Hot H_2SO_4 oxidizes it with formation of phosphorous acid and sulfur dioxide: $P_4 + 6H_2SO_4 = 4H_3PO_3 + 6SO_2$. Nitric acid oxidizes it violently to phosphoric acid and nitrogen di- and tetr-oxids: $12HNO_3 + P_4 = 4H_3PO_4 + 4N_2O_4 + 4NO$.

Phosphorus is a reducing agent. When immersed in cupric sulfate solution, it becomes covered with a coating of metallic copper. In silver nitrate solution it produces a black deposit of silver phosphid.

The principal uses of phosphorus are in making matches, rat paste and phosphor bronze.

Toxicology.—The red variety differs from the other allotropic forms of phosphorus in not being poisonous, probably owing to its insolubility, and in being little liable to cause injury by burning.

The burns produced by yellow phosphorus are more serious than a like destruction of cutaneous surface by other substances. A burning fragment of P adheres tenaciously to the skin, into which it burrows. One of the products of the combustion is metaphosphoric acid (q. v.) which, being absorbed, gives rise to true poisoning.

Burns by P should be washed immediately with dilute javelle water, liq. sodæ chlorinatæ, or solution of chlorid of lime. Yellow P should never be allowed to come in contact with the skin, except it be under cold water.

Yellow P is one of the most insidious of poisons. It is taken or administered usually as "ratsbane" or match-heads. The former is frequently starch paste, charged with phosphorus; the latter, in the ordinary sulfur match, a mixture of potassium chlorate, very fine sand, phosphorus, and a coloring matter. The symptoms in acute phosphorus-poisoning appear with greater or less rapidity, according to the dose, and the presence or absence in the stomach of substances which favor its absorption. Their appearance may be delayed for days, but as a rule they appear within a few hours. A disagreeable garlicky taste in the mouth, and heat in the stomach are first observed, the latter gradually developing into a burning pain, accompanied by vomiting of dark-colored matter, which, when shaken in the dark, is phosphorescent; low temperature and dilatation of the pupils. In some cases, death follows at this point suddenly, without the appearance of any further marked symptoms. Usually, however, the patient rallies, seems to be doing well, until, suddenly, jaundice makes its appearance, accompanied by retention of urine, and frequently delirium, followed by coma and death.

There is no known chemical antidote to phosphorus. The treatment is, therefore, limited to the removal of the unabsorbed portions of the poison by the action of an emetic, zinc or copper sulfate, or apomorphin, as expeditiously as possible, and the administration of French oil of turpentine—the older the oil the better—as a physiological antidote. The use of fixed oils or fats is to be avoided, as they favor the absorption of the poison, by their solvent action. The prognosis is very unfavorable.

Analysis.—When, after a death supposed to be caused by phosphorus, chemical evidence of the existence of the poison in the body, etc., is desired, the investigation must be made as soon after death as possible, for the reason that the element is rapidly oxidized, and the detection of the higher stages of oxidation of phosphorus is of no value as evidence of the administration of the element, because they are normal constituents of the body and of the food.

The detection of elementary phosphorus in a systematic toxicological analysis is connected with that of prussic acid, alcohol, ether, chloroform, and other volatile poisons. The substances under examination are diluted with H_2O , acidulated with tartaric acid and heated over a sand-bath in the flask *a* (Fig. 31). This flask is connected with a CO_2 generator, *c*, whose stopcock is closed, and with a Liebig's condenser, *e*, which is in darkness (the operation is best

conducted in a dark room), and so placed as to deliver the distillate into the flask, *f*. The odor of the distillate is noted. In the presence of P it is usually alliaceous. The condenser is also observed. If, at the point of greatest condensation, a luminous ring be observed (in the absence of *all* reflections), it is proof positive of the presence of unoxidized phosphorus. The absence, however, of that poison is not

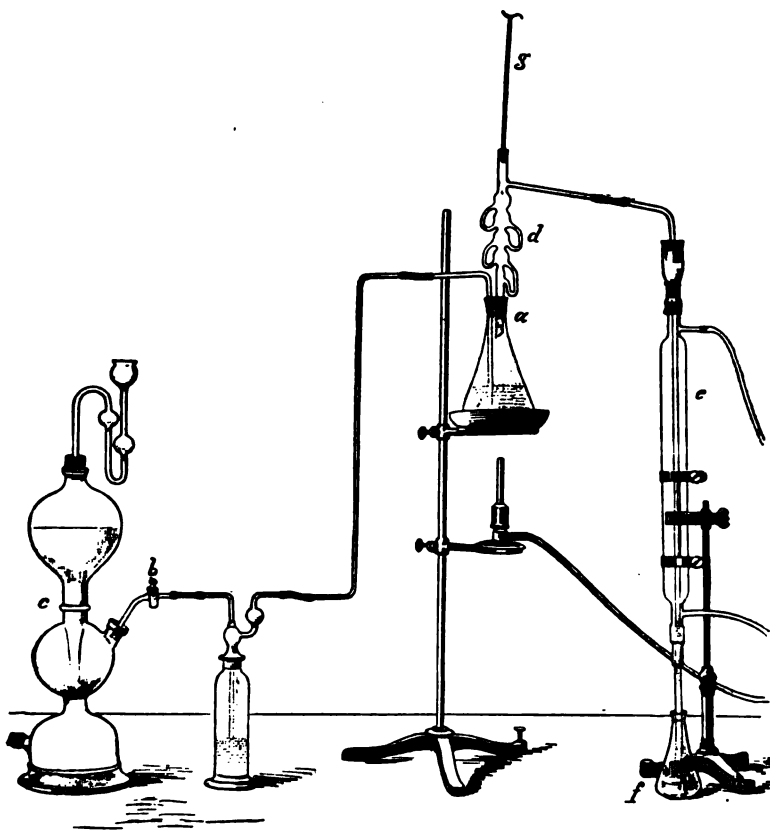


FIG. 31.

to be inferred from the absence of the luminous ring (see above). If this fail to appear, when one-third the fluid contents of the flask *a* have distilled over, the condenser is disconnected, and in its place the absorbing apparatus, Fig. 32, partly filled with a neutral solution of silver nitrate, is adjusted by a rubber tube, and a slow and constant stream of CO_2 is caused to traverse the apparatus from *c* (Fig. 31). If, during continuation of the distillation, no black deposit be formed in the silver solution, the absence of P may be

inferred. If a black deposit be formed, it must be further examined to determine if it be silver phosphid. For this purpose the apparatus shown in Fig. 33 is used. In the bottle *a* hydrogen is generated from pure Zn and H_2SO_4 , the gas passing through the drying-tube *b*, filled with fragments of CaCl_2 , and out through the platinum tip at *c*; *d* and *e* are pinch-cocks. When the apparatus is filled with H , *d* is closed until the funnel-tube *f* is three-quarters filled with the liquid from *a*; then *e* is closed and *d* opened, and the black silver deposit, which has been collected on a filter and washed, is thrown into *f*; *e* is then slightly opened and the escaping gas ignited at *c*, the size of the flame being regulated by *e*. If the deposit contain P, the flame will have a green color; and, when examined with the spectroscope, will give the spectrum of bright bands shown in Fig. 34.



FIG. 32.

Chronic phosphorus poisoning, or *Lucifer disease*, occurs among operatives engaged in the dipping, drying, and packing of phosphorus matches. Those engaged in the manufacture of phosphorus itself are not so affected. Sickly women and children are most subject to it. The cause of the disease has been ascribed to the presence of arsenic, and to the formation of oxids of phosphorus, and of ozone. The progress of the disorder is slow, and its culminating manifestation is the destruction of one or both maxillæ by necrosis.



FIG. 33.

The frequency of the disease may be in some degree diminished by thorough ventilation of the shops, by frequent washing of the face and mouth with a weak solution of sodium carbonate,

by exposing oil of turpentine in saucers in the workshops, and particularly by keeping the teeth in repair. None of these methods, however, effect a perfect prevention, which can only be attained by the substitution of the red variety of phosphorus for the yellow in this industry.

Hydrogen Phosphids.—**Gaseous hydrogen phosphid—Phosphin**—*Phosphonia*, *Phosphamin*, PH_3 —34—a colorless gas, having a strong alliaceous odor, which is obtained pure by decomposing phosphonium iodid, PH_4I , with H_2O . Mixed with H and vapor of P_2H_4 , it is produced, as a spontaneously inflammable gas, by the action of hot, concentrated solution of potassium hydroxid on P , or by decomposition of calcium phosphid by H_2O . It is highly poisonous. After death, the blood is found to be of a dark violet color, and also to have, in a great measure, lost its power of absorbing oxygen.

Liquid hydrogen phosphid— P_2H_4 —66—is the substance whose vapor communicates to PH_3 its property of igniting on contact with air. It is separated by passing the spontaneously inflammable PH_3 through a bulb tube, surrounded by a freezing mixture.

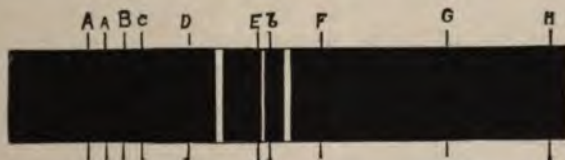


FIG. 34.

It is a colorless, heavy liquid, which is decomposed by exposure to sunlight, or to a temperature of 30° (86°F.).

Solid hydrogen phosphid— P_4H_2 —126—is a yellow solid, formed when P_2H_4 is decomposed by sunlight. It is not phosphorescent and only ignites at 160° (320°F.).

Compounds of Phosphorus with the Halogens—Phosphorus Trichlorid— PCl_3 —137.5—is obtained by heating P in a limited supply of Cl . It is a colorless liquid; sp. gr. 1.61; has an irritating odor; fumes in air; boils at 76° (169°F.). Water decomposes it with formation of H_3PO_3 and HCl .

Phosphorus Pentachlorid— PCl_5 —208.5—is formed when P is burnt in excess of Cl . It is a light yellow, crystalline solid: gives off irritating fumes; and is decomposed by H_2O .

Phosphorus Oxychlorid— POCl_3 —153.5—is formed by the action of a limited quantity of H_2O on the pentachlorid: $\text{PCl}_5 + \text{H}_2\text{O} = \text{POCl}_3 + 2\text{HCl}$. It is a colorless liquid: sp. gr. 1.07; boils at 110° (230°F.); and solidifies at -10° ($+14^\circ \text{F.}$).

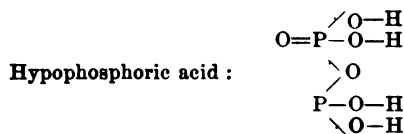
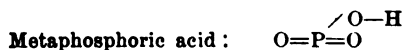
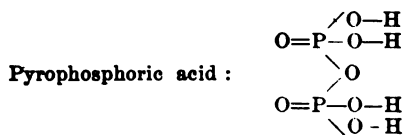
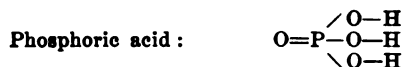
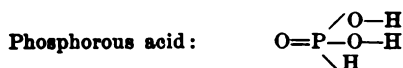
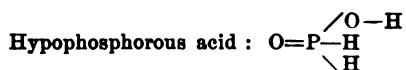
With **bromin** P forms compounds similar in composition and properties to the chlorin compounds. With **iodin** it forms two compounds, P_2I_4 and PI_3 . With **fluorin** it forms two compounds, PF_3 and PF_5 , the former liquid, the second gaseous.

Oxids of Phosphorus.—Two are known: P_2O_3 and P_2O_5 .

Phosphorus Trioxid.—*Phosphorous anhydrid, Phosphorous oxid*— P_2O_3 —110—is formed when P is burned in a very limited supply of perfectly dry air, or O. It is white, flocculent solid, which, on exposure to air, ignites by the heat developed by its union with H_2O to form phosphorous acid.

Phosphorus Pentoxid.—*Phosphoric anhydrid, Phosphoric oxid*.— P_2O_5 —142—is formed when P is burned in an excess of dry O. It is a white, flocculent solid, which has almost as great a tendency to combine with H_2O as has P_2O_3 . It absorbs moisture rapidly, deliquescent to a highly acid liquid, containing, not phosphoric, but metaphosphoric acid. It is used as a drying agent.

Phosphorus Acids.—Six oxyacids of phosphorus are known :



Only those H atoms which are connected with the P atoms through O atoms are basic. Hence H_3PO_2 is monobasic; H_3PO_3 is dibasic; H_3PO_4 is tribasic; $H_4P_2O_7$ is tetrabasic; HPO_2 is monobasic, and $H_4P_2O_6$ is tetrabasic. Pyrophosphorous acid, $O=P_2 \equiv (OH)_4$ is only known in an organic derivative, acetyl-pyrophosphorous acid : $O=P_2 \equiv H.O(C_2H_3O).(OH)_2$; and metaphosphorous acid, $O=P \equiv O.OH$ is unknown.

Hypophosphorous Acid.— H_3PO_2 —66—is a crystalline solid, or, more usually, a strongly acid, colorless syrup. It is oxidized by air to a mixture of H_3PO_3 and H_3PO_4 .

The hypophosphites, as well as the free acid, are powerful reducing agents.

Phosphorous Acid— H_3PO_3 —82—is formed by decomposition of phosphorus trichlorid by water: $\text{PCl}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCl}$. It is a highly acid syrup, is decomposed by heat, and is a strong reducing agent.

Phosphoric Acid—*Orthophosphoric acid*—*Common or tribasic phosphoric acid*—**Acidum phosphoricum** (U. S.; Br.)— H_3PO_4 —98—does not occur free in nature, but is widely disseminated in combination, in the phosphates, in the three kingdoms of nature.

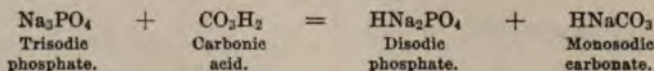
It is prepared: (1) By converting bone phosphate, $\text{Ca}_3(\text{PO}_4)_2$ into the corresponding lead or barium salt, $\text{Pb}_3(\text{PO}_4)_2$ or $\text{Ba}_3(\text{PO}_4)_2$, and decomposing the former by H_2S , or the latter by H_2SO_4 . (2) By oxidizing P by dilute HNO_3 , aided by heat. The operation should be conducted with caution, and heat gradually applied by the sand bath. It is best to use red phosphorus. This is the process directed by the U. S. and Br. Pharm.

The concentrated acid is a colorless, transparent, syrupy liquid; still containing H_2O , which it gives off on exposure over H_2SO_4 , leaving the pure acid, in transparent, deliquescent, prismatic crystals. It is decomposed by heat to form, first, pyrophosphoric acid, then metaphosphoric acid. It is tribasic.

If made from arsenical phosphorus, and commercial phosphorus is arsenical unless made by the electrolytic method (p. 160), it is contaminated with arsenic acid, whose presence may be recognized by Marsh's test (q. v.). The acid should not respond to the indigo and ferrous sulfate tests for HNO_3 .

Ortho-acids are those in which the number of hydroxyls equals the valence of the acidulous elements. Thus orthophosphoric acid is $\text{P}(\text{OH})_5$; orthocarbonic acid, $\text{C}(\text{OH})_4$. Sometimes, as in the case of phosphorus, when this acid is not known, that in which the number of hydroxyls most nearly equals the valence of the acidulous element is, improperly, called the ortho-acid.

Phosphates.—Phosphoric acid being tribasic, the phosphates have the composition $\text{M}'\text{H}_2\text{PO}_4$; $\text{M}'_2\text{HPO}_4$; $\text{M}'_3\text{PO}_4$; $\text{M}''(\text{H}_2\text{PO}_4)_2$; $\text{M}''_2(\text{HPO}_4)_2$; $\text{M}''_3(\text{PO}_4)_2$; $\text{M}'''\text{M}'\text{PO}_4$; and $\text{M}''' \text{PO}_4$. The monometallic salts are all soluble and are strongly acid. Of the dimetallic salts, those of the alkali metals only are soluble and their solutions are faintly alkaline; the others are unstable, and exhibit a marked tendency to transformation into monometallic or trimetallic salts. The normal phosphates of the alkali metals are the only soluble trimetallic phosphates. Their solutions are strongly alkaline, and they are decomposed even by weak acids:



All the monometallic phosphates, except those of the alkali metals, are decomposed by ammonium hydroxid, with precipitation of the corresponding trimetallic salt.

Analytical Characters.—(1) With ammoniacal solution of silver nitrate, a yellow precipitate. (2) With solution of ammonium molybdate in HNO_3 , a yellow precipitate. (3) With magnesia mixture,* a white, crystalline precipitate, soluble in acids, insoluble in ammonium hydroxid.

Pyrophosphoric Acid— $\text{H}_4\text{P}_2\text{O}_7$ —178.—When phosphoric acid (or hydro-disodic phosphate) is maintained at 213° (415.4°F.), two of its molecules unite, with the loss of the elements of a molecule of water: $2\text{H}_3\text{PO}_4 = \text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$, to form pyrophosphoric acid.

Metaphosphoric Acid—*Glacial phosphoric acid*— HPO_3 —80—is formed by heating H_3PO_4 or $\text{H}_4\text{P}_2\text{O}_7$ to near redness: $\text{H}_3\text{PO}_4 = \text{HPO}_3 + \text{H}_2\text{O}$; or $\text{H}_4\text{P}_2\text{O}_7 = 2\text{HPO}_3 + \text{H}_2\text{O}$. It is usually obtained from bone phosphate; this is first converted into ammonium phosphate, which is then subjected to a red heat.

It is a white, glassy, transparent solid, odorless and acid in taste and reaction. Slowly deliquescent in air, it is very soluble in H_2O , although the solution takes place slowly, and is accompanied by a peculiar crackling sound. In constitution and basicity it resembles HNO_3 .

The metaphosphates are capable of existing in five polymeric modifications (see polymerism): Mono- di- tri- tetra- and hexmeta- phosphates: $\text{M}'\text{PO}_3$; $\text{M}'_2(\text{PO}_3)_2$ and $\text{M}''(\text{PO}_3)_2$; $\text{M}'_3(\text{PO}_3)_3$; $\text{M}'_4(\text{PO}_3)_4$ and $\text{M}''_2(\text{PO}_3)_4$; and $\text{M}'_6(\text{PO}_3)_6$.

Hypophosphoric Acid— $\text{H}_4\text{P}_2\text{O}_6$ —162.—When phosphorus is exposed to moist air a strongly acid liquid is slowly formed, known as **phosphatic acid**. This is a mixture of phosphorous, phosphoric and hypophosphoric acids. The last named is separated from the others by taking advantage of the sparing solubility of its acid sodium salt; this is then converted into the lead salt, which is decomposed by H_2S , and the liberated acid concentrated. It has not been crystallized. It is quite stable at the ordinary temperature, but slowly decomposes to a mixture of phosphorous and pyrophosphoric acids. It is quadribasic. It may be considered as formed by the union of a molecule of phosphoric acid and one of phosphorous acid, with loss of H_2O : $\text{H}_3\text{PO}_4 + \text{H}_3\text{PO}_3 = \text{H}_4\text{P}_2\text{O}_6 + \text{H}_2\text{O}$.

Action of the Phosphates on the Economy.—The salts of phos-

* Made by dissolving 11 pts. crystallized magnesium chlorid and 28 pts. ammonium chlorid in 130 pts. water, adding 70 pts. dilute ammonium hydroxid (sp. gr. 0.96) and filtering after two days.

phoric acid are important constituents of animal tissues, and give rise, when taken internally, in reasonable doses, to no untoward symptoms. The acid itself may act deleteriously, by virtue of its acid reaction. Meta- and pyrophosphoric acids, even when taken in the form of neutral salts, have a distinct action (the pyro being the more active) upon the motor ganglia of the heart, producing diminution of the blood-pressure, and, in comparatively small doses, death from cessation of the heart's action.

ARSENIC.

Symbol=As—*Atomic weight*=75 (O=16:75; H=1:74.4)—*Molecular weight*=300 (As₄)—*Sp. gr. of solid; crystalline*=5.75, *amorphous*=4.71; *of vapor*=10.6 *A* at 860° (1580° F.)—*Name from* ἀρσενικόν=*orpiment*.

Occurrence.—Free in small quantity; in combination as arsenides of Fe, Co, and Ni, but most abundantly in the sulfids, orpiment and realgar, and in arsenical iron pyrites, or mispickel.

Preparation.—(1) By heating mispickel in clay cylinders, which communicate with sheet iron condensing tubes.

(2) By heating a mixture of arsenic trioxid and charcoal; and purifying the product by resublimation.

Properties.—*Physical.*—A brittle, crystalline, steel-gray solid, having a metallic luster, or a dull, black, amorphous powder. At the ordinary pressure, and without contact of air, it volatilizes without fusion at 180° (356° F.); under strong pressure it fuses at a dull red heat. Its vapor is yellowish, and has the odor of garlic. It is insoluble in H₂O, and in other liquids unless chemically altered.

Chemical.—Heated in air it is converted into the trioxid, and ignites somewhat below a red heat. In O it burns with a brilliant, bluish-white light. In dry air it is not altered, but in the presence of moisture its surface becomes tarnished by oxidation. In H₂O it is slowly oxidized, a portion of the oxid dissolving in the water. It combines readily with Cl, Br, I, and S, and with most of the metals. With H it only combines when that element is in the nascent state. Warm, concentrated H₂SO₄ is decomposed by As, with formation of SO₂, As₂O₃, and H₂O. Nitric acid is readily decomposed, giving up its O to the formation of arsenic acid. With hot HCl, arsenic trichlorid is formed. When fused with potassium hydroxid, arsenic is oxidized, H is given off, and a mixture of potassium arsenite and arsenid remains, which by greater heat is converted into arsenic, which volatilizes, and potassium arsenate, which remains.

Elementary arsenic enters into the composition of fly poison and of

shot, and is used in the manufacture of certain pigments and fire-works.

Compounds of Arsenic and Hydrogen.—Two are known: the solid As_2H (?) and the gaseous, AsH_3 .

Hydrogen Arsenid—Arsin—Arseniuretted or arsenetted hydrogen—Arsenia—Arsenamin— AsH_3 —Molecular weight=78—Sp. gr.=2.695 A—Liquefies at -40° (-40° F.).

Formation.—(1) By the action of H_2O upon an alloy, obtained by fusing together native sulfid of antimony, 2 pts.; cream of tartar, 2 pts.; and arsenic trioxid, 1 pt.

(2) By the action of dilute HCl or H_2SO_4 upon the arsenids of Zn and Sn. This is practically the same as 3, nascent hydrogen being formed by the action of the metal upon the acid.

(3) Whenever a reducible compound of arsenic is in presence of nascent hydrogen. (See Marsh test.)

(4) By the action of H_2O upon the arsenids of the alkali metals.

(5) By the combined action of air, moisture and organic matter upon arsenical pigments.

(6) By the action of hot solution of potassium hydroxid upon reducible compounds of As in the presence of zinc.

Properties.—Physical.—A colorless gas; having a strong alliaceous odor; soluble in 5 vols. of H_2O , free from air.

Chemical.—It is neutral in reaction. In contact with air and moisture its H is slowly removed by oxidation, and elementary As deposited. It is also decomposed into its elements by the passage through it of luminous electric discharges; and when subjected to a red heat. It is acted on by dry O at ordinary temperatures with the formation of a black deposit, which is at first solid hydrogen arsenid, later elementary As. A mixture of AsH_3 and O, containing 3 vols. O and 2 vols. AsH_3 , explodes when heated, forming As_2O_3 and H_2O . If the proportion of O be less, elementary As is deposited.

The gas burns with a greenish flame, from which a white cloud of arsenic trioxid arises. A cold surface, held above the flame, becomes coated with a white, crystalline deposit of the oxid. If the flame be cooled, by the introduction of a cold surface into it, the H alone is oxidized, and elementary As is deposited. Chlorin decomposes the gas explosively, with formation of HCl and arsenic, or arsenic trichlorid, if the Cl be in excess. In the presence of H_2O , arsenous and arsenic acids are formed. Bromin and iodine behave similarly, but with less violence.

All oxidizing agents decompose it readily; H_2O and arsenic trioxid being formed by the less active oxidants, and H_2O and arsenic acid by the more active. Solid potassium hydroxid decomposes the

gas partially, and becomes coated with a dark deposit, which seems to be elementary arsenic. Solutions of the alkaline hydroxids absorb and decompose it; H is given off and an alkaline arsenite remains in the solution. Many metals, when heated in H_3As , decompose it with formation of a metallic arsenid and liberation of hydrogen. Solution of silver nitrate is reduced by it; elementary silver is deposited, and the solution contains silver arsenite.

Although H_2S and H_3As decompose each other to a great extent, with formation of arsenic trisulfid, in the presence of air, the two gases do not act upon each other at the ordinary temperature, even in the direct sunlight, either dry or in the presence of H_2O , when air is absent. Hence in making H_2S for use in toxicological analysis, materials free from As must be used; or the H_2S must be purified as described on p. 139.

Compounds of Arsenic with the Halogens.—**Arsenic Trifluorid**— AsF_3 —132.—A colorless, fuming liquid, boiling at 63° (145° F.), obtained by distilling a mixture of As_2O_3 , H_2SO_4 , and fluorspar. It attacks glass.

Arsenic Trichlorid— $AsCl_3$ —181.5.—Obtained by distilling a mixture of As_2O_3 , H_2SO_4 , and NaCl, using a well-cooled receiver.

It is a colorless liquid, boils at 134° (273° F.), fumes when exposed to the air, and volatilizes readily at temperatures below its boiling point. Its formation must be avoided in processes for the chemico-legal detection of arsenic, lest it be volatilized and lost. It is formed by the action of HCl, even when comparatively dilute, upon As_2O_3 at the temperature of the water-bath; but, if potassium chlorate be added, the trioxid is oxidized to arsenic acid, and the formation of the chlorid thus prevented. Arsenic trioxid, when fused with sodium nitrate, is converted into sodium arsenate, which is not volatile. If, however, small quantities of chlorids be present, $AsCl_3$ is formed. It is highly poisonous.

Arsenic Tribromid— $AsBr_3$ —315.—Obtained by adding powdered As to Br, and distilling the product at 220° (428° F.). A solid, colorless, crystalline body, fuses at 20° – 25° (68° – 77° F.), boils at 220° (428° F.), and is decomposed by H_2O .

Arsenic Triiodid—*Arsenii iodidum*, U. S.— AsI_3 —456.—Formed by adding As to a solution of I in carbon bisulfid, or by fusing together As and I in proper proportions. A brick-red solid, fusible and volatile. Soluble in a large quantity of H_2O . Decomposed by a small quantity of H_2O into HI, As_2O_3 , H_2O and a residue of AsI_3 .

Compounds of Arsenic and Oxygen.—Two are known: As_2O_3 and As_2O_5 .

Probably the gray substance formed by the action of moist air on elementary arsenic is a lower oxid.

Arsenic Trioxid—*Arsenous anhydrid*—*Arsenous oxid*—*White arsenic*—*Arsenic*—*Arsenous acid*—**Acidum arseniosum**, U. S.; Br. — As_2O_3 —198.

Preparation.—(1) By roasting the native sulfids of arsenic in a current of air.

(2) By burning arsenic in air or oxygen.

Properties.—*Physical.*—It occurs in three forms: *crystallized* or "*powdered*," *vitreous*, and *porcelainous*. When freshly fused, it appears in colorless or faintly yellow, translucent, vitreous masses, having no visible crystalline structure. Shortly, however, these masses become opaque upon the surface, and present the appearance of porcelain. This change slowly progresses toward the center of the mass, which, however, remains vitreous for a long time. When arsenic trioxid, is sublimed, if the vapors be condensed upon a cool surface, it is deposited in the form of brilliant octahedral crystals, which are larger and more perfect the nearer the temperature of the condensing surface is to 180° (356° F.). When sublimed under slightly increased pressure, or in an atmosphere of SO_2 , right rhombic prisms occur among the octahedra. It is therefore dimorphous. The crystalline variety may be converted into the vitreous, by keeping it for some time at a temperature near its point of volatilization.

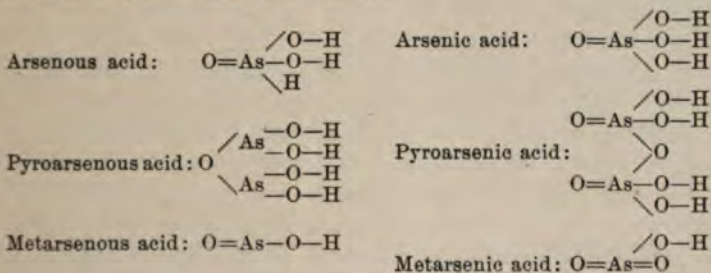
Although As_2O_3 is heavier than water, when thrown upon that liquid a large part of the crystalline powder floats, and a part of that which sinks at first subsequently rises. This is due to adhesion of air to the particles of the solid. The same phenomenon renders the solution of As_2O_3 in water slow and irregular. The vitreous variety is more readily soluble than the crystalline. The taste of arsenic trioxid in solution is very faint, at first sweetish, afterward very slightly metallic. The solid is almost tasteless. It is odorless. In aqueous solution it has a faintly acid reaction. The sp. gr. of the vitreous variety is 3.785; that of the crystalline, 3.689.

Chemical.—Its solutions are acid in reaction, and probably contain the true arsenous acid, H_3AsO_3 . They are neutralized by bases, with formation of **arsenites**. Solutions of sodium, or potassium hydroxid, or carbonate dissolve it, with formation of the corresponding arsenite. It is readily reduced, with separation of As, when heated with hydrogen, carbon, and potassium cyanid, and at lower temperatures by more active reducing agents. Oxidizing agents, such as HNO_3 , the chlorin oxyacids, chromic acid, convert it into arsenic pentoxid or arsenic acid. Its solution, acidulated with HCl and boiled in presence of copper, deposits on the metal a gray film, composed of an alloy of Cu and As.

Arsenic Pentoxid—*Arsenic anhydrid*—*Arsenic oxid*— As_2O_5 —230 —is obtained by heating arsenic acid to redness. —It is a white, amor-

phous solid, which, when exposed to the air, slowly absorbs moisture. It is fusible at a dull red heat, and at a slightly higher temperature decomposes to As_2O_3 and O_2 . It dissolves slowly in H_2O , forming arsenic acid, H_3AsO_4 .

Arsenic Acids.—The oxyacids of arsenic form a series, corresponding to that of the oxyacids of phosphorus, except that the hypoarsenous and hypoarsenic acids are unknown, and pyro- and metarsenous acids are known in their salts:



Arsenous Acid.— H_3AsO_3 —126—exists in aqueous solutions of the trioxid, although it has not been separated. Corresponding to it are important salts, called **arsenites**, which have the general formulæ $\text{HM}'_2\text{AsO}_3$, $\text{HM}''\text{AsO}_3$, $\text{H}_4\text{M}''(\text{AsO}_3)_2$. Pyro- and metarsenous acids are only known in combination.

Arsenic Acid—Orthoarsenic acid— H_3AsO_4 —142—is obtained by oxidizing As_2O_3 with HNO_3 in the presence of H_2O : $\text{As}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{HNO}_3 = 2\text{H}_3\text{AsO}_4 + \text{N}_2\text{O}_3$. A similar oxidation is also effected by Cl , aqua regia, and other oxidants.

A syrupy, colorless, strongly acid solution is thus obtained, which, at 15° (59°F.), becomes semi-solid, from the formation of transparent crystals, containing 1 Aq. These crystals, which are very soluble and deliquescent, lose their Aq at 100° (212°F.), and form a white, pasty mass, composed of minute white, anhydrous needles. At higher temperatures it is converted into $\text{H}_4\text{As}_2\text{O}_7$, HAsO_3 , and As_2O_5 . In presence of nascent H it is decomposed into H_2O and AsH_3 . It is reducible to H_3AsO_3 by SO_2 .

The action of H_2S upon acid solutions of arsenic acid, or of the arsenates, varies with the rapidity of the action and the temperature at which it occurs. With a slow current of H_2S , at a low temperature, no precipitate is formed, and the solution remains colorless. Under these conditions **thioxyarsenic acid**, $\text{H}_3\text{AsO}_3\text{S}$, is formed: $\text{H}_3\text{AsO}_4 + \text{H}_2\text{S} = \text{H}_3\text{AsSO}_3 + \text{H}_2\text{O}$. By a further action of H_2S , arsenic pentasulfid is formed: $2\text{H}_3\text{AsO}_3\text{S} + 3\text{H}_2\text{S} = \text{As}_2\text{S}_5 + 6\text{H}_2\text{O}$. If the current of H_2S be very slow, the thioxyarsenic acid produced is decomposed according to the equation: $2\text{H}_3\text{AsO}_3\text{S} = \text{As}_2\text{O}_3 + 3\text{H}_2\text{O} + \text{S}_2$ and

the precipitate then produced consists of a mixture of As_2S_3 , As_2S_5 and S.

Like phosphoric acid, arsenic acid is tribasic; and the arsenates resemble the phosphates in composition, and in many of their chemical and physical properties.

Pyroarsenic Acid— $\text{H}_4\text{As}_2\text{O}_7$ —266.—Arsenic acid, when heated to 160° (320°F.), is converted into compact masses of pyroarsenic acid: $2\text{H}_3\text{AsO}_4 = \text{H}_4\text{As}_2\text{O}_7 + \text{H}_2\text{O}$. It is very prone to revert to arsenic acid, by taking up water.

Metarsenic Acid— HAsO_3 —124.—At 200° – 206° (392° – 403°F.) $\text{H}_4\text{As}_2\text{O}_7$ gradually loses H_2O to form metarsenic acid: $\text{H}_4\text{As}_2\text{O}_7 = 2\text{HAsO}_3 + \text{H}_2\text{O}$. It forms white, pearly crystals, which dissolve readily in H_2O , with regeneration of H_3AsO_4 . It is monobasic.

Compounds of Arsenic and Sulfur.—**Arsenic Bisulfid**—*Red sulfid of arsenic*—*Realgar*—*Red orpiment*—*Ruby sulfur*—*Sandarach*— As_2S_2 —214—occurs in nature, in translucent, ruby-red crystals. It is also prepared by heating a mixture of As_2O_3 and S. As so obtained it appears in brick-red masses.

It is fusible, insoluble in H_2O , but soluble in solutions of the alkaline sulfids, and in boiling solution of potassium hydroxid.

Arsenic Trisulfid—*Orpiment*—*Auripigmentum*—*Yellow sulfid of arsenic*—*King's yellow*— As_2S_3 —246—occurs in nature in brilliant golden yellow flakes. Obtained by passing H_2S through an acid solution of As_2O_3 ; or by heating a mixture of As and S, or of As_2O_3 and S in equivalent proportions.

When formed by precipitation, it is a lemon-yellow powder; or in orange-yellow, crystalline masses, when prepared by sublimation. Almost insoluble in cold H_2O , but sufficiently soluble in hot H_2O to communicate to it a distinct yellow color. By continued boiling with H_2O it is decomposed into H_2S and As_2O_3 . Insoluble in dilute HCl ; but readily soluble in solutions of the alkaline hydroxids, carbonates, and sulfids. It volatilizes when heated.

Nitric acid oxidizes it, forming H_3AsO_4 and H_2SO_4 . A mixture of HCl and potassium chlorate has the same effect. It corresponds in constitution to As_2O_3 , and like it, may be regarded as an anhydrid, for although thioarsenous acid, H_3AsS_3 , has not been separated, the thioarsenites, pyro- and meta-thioarsenites are well-characterized compounds.

Arsenic Pentasulfid— As_2S_5 —310—is formed by fusing a mixture of As_2S_3 and S in proper proportions, and, by the prolonged action of H_2S , at low temperatures, upon solutions of the arsenates.

It is a yellow, fusible solid, capable of sublimation in absence of air. There exist well-defined thioarsenates, pyro- and meta-thioarsenates.

Action of Arsenical Compounds Upon the Animal Economy.

The poisonous nature of many of the arsenical compounds has been known from remote antiquity, and it is probable that more murders have been committed by their use than by that of all other toxic substances combined. Even at the present time—notwithstanding the fact that, suspicion once aroused, the detection of arsenic in the dead body is certain and comparatively easy—criminal arsenical poisoning is still quite common, especially in rural districts.

The poison is usually taken by the mouth, but it has also been introduced by other channels; the skin, either uninjured or abraded, the rectum, vagina, and male urethra. The forms in which it has been taken are: (1) **Elementary arsenic**, which is not poisonous so long as it remains such. In contact with water, or with the saliva, however, it is converted into an oxid, which is then dissolved, and, being capable of absorption, produces the characteristic effects of the arsenical compounds. Certain fly-papers and fly-poisons contain As, a portion of which has been oxidized by the action of air and moisture. (2) **Hydrogen arsenid**, the most actively poisonous of the inorganic compounds of arsenic, has been the cause of several accidental deaths, among others, that of the chemist Gehlen, who died in consequence of having inhaled the gas while experimenting with it. In other cases death has followed the inhalation of hydrogen, made from zinc and sulfuric acid contaminated with arsenic. (3) **Arsenic trioxid** is the compound most frequently used by criminals. It has been given by every channel of entrance to the circulation; in some instances concealed with great art, in others merely held in suspension by stirring in a transparent fluid, given to an intoxicated person. If the poison have been in quantity, and undissolved, it may be found in the stomach after death, in the form of eight-sided crystals, more or less worn by the action of the solvents with which it has come in contact. (4) **Potassium arsenite**, the active substance in "Fowler's solution," although largely used by the laity in malarial districts as an *ague-cure*, has, so far as the records show, produced but few cases of fatal poisoning. (5) **Sodium arsenite** is sometimes used to clean metal vessels, a practice whose natural results are exemplified in the death of an individual who drank beer from a pewter mug so cleaned; and in the serious illness of 340 children in an English institution, in which this material had been used for cleaning the water-boiler. (6) **Arsenic acid and arsenates**.—The acid itself has, so far as we know, been directly fatal to no one. The cases of death and illness, however, which have been put to the account of the red anilin dyes, are not due to them directly.

but to arsenical residues remaining in them as the result of defective processes of manufacture. (7) **Sulfids of arsenic.**—Poisoning by these is generally due to the use of orpiment, introduced into articles of food as a coloring matter, by a combination of fraud and stupidity, in mistake for turmeric. (8) **The arsenical greens.**—Scheele's green, or cupric arsenite, and Schweinfurth green, or cupric acetometarsenite (the latter commonly known in the United States as **Paris green**, a name applied in Europe to one of the anilin pigments). These substances, although rarely administered with murderous intent, have been the cause of death in a great number of cases.

The arsenical pigments may also produce disastrous results by "accident;" by being incorporated in ornamental pieces of confectionery; by being used in the coloring of textile fabrics, from which they may be easily rubbed off; from their use for the destruction of insects, and by being used in the manufacture of wall-paper. Many instances of chronic or subacute arsenical poisoning have resulted from inhabiting rooms hung with paper whose whites, reds, or greens were produced by arsenical pigments. From such paper the poison is disseminated in the atmosphere of the room in two ways: either as an impalpable powder, mechanically detached from the paper and floating in the air, or by their decomposition, and the consequent diffusion of volatile arsenical compounds in the air.

The treatment in acute arsenical poisoning is the same, whatever may be the form in which the poison has been taken, if it have been taken by the mouth. The first indication is the removal of any unabsorbed poison from the alimentary canal. If vomiting have not occurred from the effects of the toxic, it should be induced by the administration of zinc sulfate, or by mechanical means. When the stomach has been emptied, the chemical antidote is to be administered, with a view to the transformation, in the stomach, of any remaining arsenical compound into the insoluble, and therefore innocuous, ferrous arsenate. To prepare the antidote, a solution of ferric sulfate, *Liq. ferri tersulphatis* (U. S.)=*Liq. ferri persulphatis* (Br) is to be diluted with three volumes of water, and treated with aqua ammoniæ in slight excess. The precipitate formed is then collected upon a muslin filter, and washed with water until the washings are nearly tasteless. The contents of the filter—*Ferri oxidum hydratum* (U. S.), *Ferri peroxidum humidum* (Br.) are to be given moist, in repeated doses of one to two teaspoonsful, until an amount of the hydrate equal to 20 times the weight of white arsenic taken has been administered. Dialyzed iron may be given while the hydrate is in preparation, or whenever the materials for its preparation are not obtainable.

Precautions to be taken by the Physician in cases of Suspected Poisoning.

It will rarely happen that in a case of suspected homicidal poisoning by arsenic, or by other poisons, the physician in charge will be willing or competent to conduct the chemical analysis, upon which, probably, the conviction or acquittal of the accused will mainly depend. Upon his knowledge and care, however, the success or futility of the chemist's labors depends in a great measure.

It is, as a rule, the physician who first suspects foul play; and while it is undoubtedly his duty to avoid any public manifestation of his suspicion, it is as certainly his duty toward his patient and toward the community, to satisfy himself as to the truth or falsity of his suspicion by the application of a simple test to the excreta of the patient during life, the result of which may enable him to prevent a crime, or, failing that, take the first step toward the punishment of the criminal.

In a case in which, from the symptoms, the physician suspects poisoning by any substance, he should himself test the urine or feces, or both, and govern his treatment and his actions toward the patient, and those surrounding the patient, by the results of his examination. Should the case terminate fatally, he should at once communicate his suspicions to the prosecuting officer, and require a post-mortem investigation, which should, if at all possible, be conducted in the presence of the chemist who is to conduct the analysis. For, be the physician as skilled as he may, there are odors and appearances, observable in many cases at the opening of the body, full of meaning to the toxicological chemist, which are ephemeral, and whose bearing upon the case is not readily recognized by those not thoroughly experienced.

Cases frequently arise in which it is impossible to bring the chemist upon the ground in time for the autopsy. In such cases the physician should remember that that portion of the poison remaining in the alimentary tract (we are speaking of true poisons) is but the residue of the dose in excess of that which has been necessary to produce death; and, if the processes of elimination have been active, there may remain no trace of the poison in the alimentary canal, while it still may be detectable in the deeper-seated organs. The poison may also have been administered by another channel than the mouth, in which event it may not reach the stomach.

For these reasons it is not sufficient to send the stomach alone for analysis. The chemist should also receive the entire intestinal canal, the liver, the spleen, one or both kidneys, a piece of muscular tissue from the leg, the brain, and any urine that may remain

in the bladder. The intestinal canal should be removed and sent to the chemist *without having been opened*, and with ligatures, enclosing the contents, at the two ends of the stomach and at the lower end of the intestine. The brain and alimentary canal are to be placed in separate jars, and the other viscera in another jar together; the urine in a vial by itself. All of these vessels are to be new and clean, and are to be closed by new corks, or by glass stoppers, or covers (not zinc screw-caps), which are then coated with paraffin (not sealing-wax), and so fastened with strings and seals, that it is impossible to open the vessels without cutting the strings or breaking the seals. Any vomited matters are to be preserved. If the physician fail to observe these precautions, he has probably made the breach in the evidence through which the criminal will escape, and has at the outset defeated the aim of the analysis.

Analytical Characters of the Arsenical Compounds.—Arsenous Compounds.—(1) H_2S , a yellow color in neutral or alkaline liquids; a yellow ppt. in acid liquids. The ppt. dissolves in solutions of the alkaline hydroxids, carbonates and sulphydrates; but is scarcely affected by HCl . Hot HNO_3 decomposes it.

(2) AgNO_3 , in the presence of a little NH_4HO , gives a yellow ppt. This test is best applied by placing the neutral arsenical solution in a porcelain capsule, adding neutral solution of AgNO_3 , and blowing upon it over the stopper of the NH_4HO bottle, moistened with that reagent.

(3) CuSO_4 under the same conditions as in (2) gives a yellowish green ppt.

(4) A small quantity of solid As_2O_3 is placed in the point *a* of the tube, Fig. 35; above it, at *b*, a splinter of recently ignited charcoal; *b* is first heated to redness, then *a*; the vapor of As_2O_3 , passing over the hot charcoal, is reduced, and elementary As is deposited at *c* in a metallic ring. The tube is then cut between *a* and *c*, the larger piece held with *d* uppermost and heated at *c*; the deposit is volatilized, the odor of garlic is observed, and bright, octahedral crystals (Fig. 37) appear in the cool part of the tube.

(5) **Reinsch Test.**—The suspected liquid is acidulated with one-sixth its bulk of HCl . Strips of electrotype copper are immersed in the liquid, which is boiled. In the presence of an arsenous compound, a gray or bluish deposit is formed upon the Cu . A similar



FIG. 35.

deposit is produced by other substances (S, Au, Pt, Bi, Sb, Hg). To complete the test the Cu is removed, washed, and dried between folds of filter paper, without removing the deposit. The copper, with its adherent film, is rolled into a cylinder, and introduced into a dry piece of Bohemian tubing, about one-fourth inch in diameter and six inches long, which is held at the angle shown in Fig. 36 and heated at the point containing the copper. If the deposit consist of arsenic, a white deposit is formed at *a*, which contains brilliant specks, and, when examined with a magnifier, is found to consist entirely of minute octahedral crystals (Fig. 37).

If the stain upon the copper, formed in the first part of the reaction, have been caused by S, Au, Pt, or Bi, no sublimate is produced during the subsequent heating in the glass tube, as the product of oxidation of sulfur is gaseous, Au and Pt are neither oxidized nor volatilized, and Bi is oxidized, but its oxid is not volatile. Sublimates are, however, formed from deposits caused by Sb or Hg, which



FIG. 36.

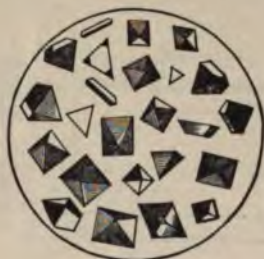


FIG. 37.

differ from that produced by arsenic in the following respects: That from Sb consists of Sb_2O_3 , which, although isodimorphous with As_2O_3 , does not crystallize under these conditions, except, sometimes, to form prismatic crystals at the heated part of the tube, or an occasional octahedral crystal beyond. The sublimate is entirely, or almost entirely amorphous, or granular, possibly containing one or two octahedral crystals, whose borders are darker than those of As_2O_3 . The sublimate from Hg consists of microscopic globules of the liquid metal. Reinsch's reaction is, therefore, a test for antimony and mercury, as well as for arsenic.

The advantages of this test are: it may be applied in the presence of organic matter, to the urine for instance; it is easily conducted; and its positive results are not misleading, *if the test be carried to completion*. These advantages render it the most suitable method for the physician to use, *during the life of the patient*. It should not be used *after death* by the physician, as by it copper is introduced into the substances under examination, which may subsequently interfere seriously with the analysis. The purity of the Cu and HCl must be

proved by a blank testing before use. Reinsch's test is not as delicate as Marsh's, and it only reacts slowly and imperfectly when the arsenic is in the higher stage of oxidation, or in presence of oxidizing agents.

(6) **Marsh's test** is based upon the formation of AsH_3 when a reducible compound of arsenic is in presence of nascent H ; and the subsequent decomposition of the arsenical gas by heat, with separation of elementary arsenic.

The apparatus used (Fig. 38) consists of a glass generating vessel, *a*, of about 150 cc. capacity, provided with a funnel-tube having a stop-cock, and a lateral outlet, either fitted in with a cork, or, better, ground in. The lateral outlet is connected with a tube, *b*, filled with fragments of calcium chlorid; which in turn connects with the

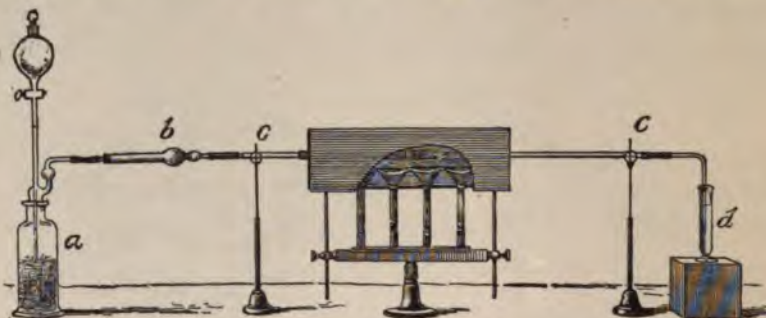


FIG. 38.

Bohemian glass tube *cc*, which should be about 0.5 cent. in diameter, and about 80 cent. long. The tube is protected by a tube of wire gauze, within which it is adjusted in the furnace as shown in the figure. The other end of *cc* is bent downward, and dips into a solution of silver nitrate in the test-tube, *d*.

The vessel *a* is first charged with about 25 grams of an alloy of pure granulated zinc, with a small quantity of platinum. The apparatus is then connected gas-tight, and the funnel tube about half filled with H_2SO_4 , diluted with an equal bulk of H_2O , and cooled. By opening the stopcock, the acid is brought in contact with the zinc in small quantities, in such a manner that during the entire testing bubbles of gas pass through *d* at the rate of 60-80 per minute. After fifteen minutes the burner is lighted, and the heating continued, during evolution of gas from zinc and H_2SO_4 , for an hour. At the end of that time, if no stain have formed in *cc* beyond the burner, the zinc and acid may be considered to be pure, and the suspected solution, which must have been previously freed from organic matter and from tin and antimony, is introduced slowly through the funnel-tube.

If arsenic be present in the substance examined, a hair-brown or gray deposit is formed in the cool part of *cc* beyond the heated part. At the same time the contents of *d* are darkened if the amount of As present is so great that all the AsH_3 produced is not decomposed in the heated portion of *cc*.

To distinguish the stains produced by arsenical compounds from the similar ones produced by antimony the following differences are noted :

The Arsenical Stain.

First. — Is farther removed from the heated portion of the tube, and, if small in quantity, is double—the first hair-brown, the second steel-gray.

Second. — Volatilizes readily when heated in an atmosphere of hydrogen, being deposited farther along in the tube. The escaping gas has the odor of garlic.

Third. — When cautiously heated in a current of oxygen, brilliant, white, octahedral crystals of arsenic trioxid are deposited farther along in the tube.

Fourth. — Instantly soluble in solution of sodium hypochlorite.

Fifth. — Slowly dissolved by solution of ammonium sulphhydrate; more rapidly when warmed.

Sixth. — The solution obtained in five leaves, on evaporation over the water-bath, a bright yellow residue.

Seventh. — The residue obtained in six is soluble in aqua ammoniæ, but insoluble in hydrochloric acid.

Eighth. — Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which turns brick-red when moistened with silver nitrate solution.

Ninth. — Is not dissolved by a solution of stannous chlorid.

The Antimonial Stain.

First. — Is quite near the heated portion of the tube. A second stain is also usually formed in front of the heated part of the tube.

Second. — Requires a much higher temperature for its volatilization; fuses before volatilizing. Escaping gas has no alliaceous odor.

Third. — No crystals formed by heating in oxygen, but an amorphous, white sublimate (see p. 179).

Fourth. — Insoluble in solution of sodium hypochlorite.

Fifth. — Dissolves quickly in solution of ammonium sulphhydrate.

Sixth. — The solution obtained in five leaves, on evaporation over the water-bath, an orange-red residue.

Seventh. — The residue obtained in six is insoluble in aqua ammoniæ, but soluble in hydrochloric acid.

Eighth. — Is soluble in warm nitric acid; the solution on evaporation yields a white residue, which is not colored when moistened with silver nitrate solution.

Ninth. — Dissolves slowly in solution of stannous chlorid.

The silver solution in *d* is tested for arsenous acid, by floating upon its surface a layer of diluted NH_4HO solution, which, in the presence of arsenic, produces a yellow (not brown) band, at the point of junction of the two liquids.

In place of bending the tube *c* downward, it may be bent upward and drawn out to a fine opening. If the escaping gas be then ignited, the heating of the tube being discontinued, a white deposit of As_2O_3

may be collected on a glass surface held *above* the flame ; or a brown deposit of elementary As upon a cold (porcelain) surface held *in* the flame.

In place of generating nascent hydrogen by the action of Zn on H_2SO_4 , it may be produced by the decomposition of acidulated H_2O by the battery, in a Marsh apparatus especially modified for that purpose.

In another modification of the Marsh test the AsH_3 is decomposed, not by passage through a red-hot tube, but by passing through a tube traversed by the spark from an induction coil.

(7) **Fresenius' and Von Babo's test.**—The sulfid, obtained in (1), is dried, and mixed with 12 parts of a *dry* mixture of 3 pts. sodium carbonate and 1 pt. potassium cyanid, and the mixture brought into a tube, drawn out to a fine opening, through which a slow current of CO_2 is allowed to pass. The tube is then heated to redness at the point containing the mixture, when, if arsenic be present, a gray deposit is formed at the constricted portion of the tube ; which has the characters of the arsenical stain indicated on p. 181.

(8) Place a small crystal of sodium sulfite in a solution of 0.3–0.4 gram of stannous chlorid in pure HCl , sp. gr. 1.13. Float the liquid to be tested on the surface of this mixture. If As be present a yellow band is formed at the junction of the two liquids, and gradually increases upwards.

ARSENIC COMPOUNDS.—(1) H_2S does not form a ppt. in neutral or alkaline solutions. In acid solutions a yellow ppt., consisting either of As_2S_3 or As_2S_5 , or a mixture of the sulfids with free S, is formed only after prolonged passage of H_2S at the ordinary temperature, more rapidly at about 70° (158°F.).

(2) AgNO_3 , under the same conditions as with the arsenous compounds, produces a brick-red ppt. of silver arsenate.

(3) CuSO_4 under like circumstances produces a bluish green ppt.

Arsenic compounds behave like arsenous compounds with the tests 4, 6 and 7 for the latter.

Method of Analysis for Mineral Poisons.—In cases of suspected poisoning a systematic course of analysis is to be followed by which the presence or absence of *all* the more usual poisons can be determined. The most advantageous process for this purpose is that of Fresenius and Van Babo, somewhat modified, in which the animal and vegetable substances are disintegrated and oxidized by a mixture of HCl and KClO_3 , and in which arsenic and antimony, if present, are separated before application of the Marsh test. For descriptions of the methods, which are somewhat intricate, the student is referred to more comprehensive works.

ANTIMONY.

Symbol=Sb (*Latin: stibium*)—*Atomic weight*=120 (O=16 : 120; H=1 : 119.04)—*Molecular weight*=(?)—*Sp. gr.*=6.175—*Fuses at* 450° (842° F.).

Occurrence.—Free in small quantity; principally in the trisulfid, Sb_2S_3 .

Preparation.—The native sulfid (black or crude antimony) is roasted, and then reduced by heating with charcoal.

Properties.—*Physical.*—A bluish gray, brittle solid, having a metallic luster; readily crystallizable; tasteless and odorless; volatilizes at a red heat, and may be distilled in an atmosphere of H.

Chemical.—Is not altered by dry or moist air at ordinary temperatures. When sufficiently heated in air, it burns, with formation of Sb_2O_3 , as a white, crystalline solid. It also combines directly with Cl, Br, I, S, and many metallic elements. It combines with H under the same circumstances as does As. Cold dilute H_2SO_4 does not affect it; the hot concentrated acid forms with it antimonyl sulfate $(\text{SbO})_2\text{SO}_4$ and SO_2 . Hot HCl dissolves it, when finely divided, with evolution of H. It is readily oxidized by HNO_3 , with formation of H_3SbO_4 or Sb_2O_4 . Aqua regia dissolves it as SbCl_3 , or SbCl_5 . Solutions of the alkaline hydroxids do not act on it.

The element does not form salts with the oxyacids. There are, however, compounds, formed by the substitution of the group antimonyl (SbO), for the basic hydrogen of those acids. (See Tartar emetic).

It enters into the composition of type metal, anti-friction metals, and britannia metal.

Hydrogen Antimonid—Stibin—Antimoniuretted hydrogen—Stibamin—Stibonia— SbH_3 —123.—It is produced, mixed with H, when a reducible compound of Sb is in presence of nascent H. It is obtained in larger amount by decomposing an alloy of 400 parts of a 2% sodium amalgam, and 8 parts of freshly reduced, and dried Sb, by H_2O , in a current of CO_2 .

It is a colorless, odorless, combustible gas, subject to the same decompositions as AsH_3 ; from which it differs in being by no means as poisonous, and in its action upon silver nitrate solution. The arsenical gas acts upon the silver salt according to the equation: $6\text{AgNO}_3 + 2\text{AsH}_3 + \text{H}_2 = \text{Ag}_2 + 2\text{Ag}_2\text{HASO}_3 + 6\text{HNO}_2$, and the precipitate formed is elementary silver, while Ag_2HASO_3 remains in the solution. In the case of SbH_3 the reaction is $3\text{AgNO}_3 + \text{SbH}_3 = 3\text{HNO}_3 + \text{SbAg}_3$, all of the Sb being precipitated in the black silver antimonid.

Chlorids of Antimony.—**Antimony Trichlorid—Protochlorid or butter of antimony— SbCl_3 —226.5**—is obtained by passing dry Cl over an excess of Sb_2S_3 ; by dissolving Sb_2S_3 in HCl; or by distilling mix-

tures, either of Sb_2S_3 and mercuric chlorid, or of Sb and mercuric chlorid, or of antimonyl pyrosulfate and sodium chlorid.

At low temperatures it is a solid, crystalline body; at the ordinary temperature a yellow, semi-solid mass, resembling butter; at 73.2° (164° F.) it fuses to a yellow, oily liquid, which boils at 223° (433.4° F.). Obtained by a solution of Sb_2S_3 in HCl of the usual strength, it forms a dark yellow solution, which, when concentrated to sp. gr. 1.47, constitutes the *Liq. Antimonii chloridi* (Br.).

It absorbs moisture from air, and is soluble in a small quantity of H_2O ; with a larger quantity it is decomposed, with precipitation of a white powder, **powder of Algaroth**, whose composition is SbOCl if cold H_2O be used, and $\text{Sb}_4\text{O}_5\text{Cl}_2$ if the H_2O be boiling. In H_2O containing 15 per cent. or more HCl , SbCl_3 is soluble without decomposition.

Antimony Pentachlorid— SbCl_5 —297.5— is formed by the action of Cl , in excess, upon Sb or SbCl_3 .

It is a fuming, colorless liquid. With a small quantity of H_2O , and by evaporation over H_2SO_4 , it forms a hydrate, $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$, which appears in transparent, deliquescent crystals. With more H_2O , a crystalline oxychlorid, SbOCl_3 , is formed; and with a still greater quantity, a white precipitate of orthoantimonic acid, H_3SbO_4 .

Compounds of Antimony and Oxygen.—Three are known, Sb_2O_3 , Sb_2O_4 and Sb_2O_5 .

Antimony Trioxid—*Antimonous anhydrid*—*Oxid of antimony*—*Antimonii oxidum* (U. S.; Br.)— Sb_2O_3 —288—occurs in nature; and is prepared artificially by decomposing the oxychlorid; or by heating Sb in air.

It crystallizes in prisms or in octahedra, and is isodimorphous with As_2O_3 , or is an amorphous, insoluble, tasteless, odorless powder; white at ordinary temperatures, but yellow when heated. It fuses readily, and may be distilled in absence of oxygen. Heated in air, it burns like tinder, and is converted into Sb_2O_4 .

It is reduced, with separation of Sb, when heated with charcoal, or in H . It is also readily oxidized by HNO_3 , or potassium permanganate. It dissolves in HCl as SbCl_3 ; in Nordhausen sulfuric acid, from which solution brilliant crystalline plates of antimonyl pyrosulfate, $(\text{SbO})_2\text{S}_2\text{O}_7$, separate; and in solutions of tartaric acid, and of hydropotassic tartrate (see Tartar emetic). Boiling solutions of alkaline hydroxids convert it into antimonic acid.

Antimony Pentoxid—*Antimonic anhydrid*— Sb_2O_5 —320—is obtained by heating metantimonic acid to dull redness. It is an amorphous, tasteless, odorless, pale lemon-yellow colored solid; very sparingly soluble in water and in acids. At a red heat it is decomposed into Sb_2O_4 and O .

Antimony Antimonate—*Intermediate oxid*—*Diantimonic tetroxid*— Sb_2O_4 —304—occurs in nature and is formed when the oxids or hydrates of Sb are strongly heated, or when the lower stages of oxidation or the sulfids are oxidized by HNO_3 , or by fusion with sodium nitrate. It is soluble in H_2O ; but is decomposed by HCl , hydropotassic tartrate, and potash.

Antimony Acids.—The normal antimonous acid, H_3SbO_3 , corresponding to H_3PO_3 , is unknown; but the series of antimonic acids: ortho, H_3SbO_4 ; pyro, $\text{H}_4\text{Sb}_2\text{O}_7$; and meta, HSbO_3 , is complete, either in the form of salts, or in that of the free acids. There also exists, in its sodium salt, a derivative of the lacking antimonous acid: **met-antimonous acid**, HSbO_2 .

The compound sometimes used in medicine under the name *washed diaphoretic antimony* is potassium metantimonate, united with an excess of the pentoxid: $2\text{KSbO}_3, \text{Sb}_2\text{O}_5$. The hydropotassic pyroantimonate, $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{Aq}$ is a valuable reagent for the sodium compounds. It is obtained by calcining a mixture of one part of antimony with four parts potassium nitrate, and fusing the product with its own weight of potassium carbonate.

Sulfids of Antimony.—**Antimony Trisulfid**—*Sesquisulfid of antimony*—*Black antimony*—**Antimonii sulfidum** (U. S.)—**Antimonium nigrum** (Br.)— Sb_2S_3 —336—is the chief ore of antimony; and is formed when H_2S is passed through a solution of tartar emetic.

The native sulfid is a steel-gray, crystalline solid; the artificial product, an orange-red, or brownish red, amorphous powder. The **crude antimony** of commerce is in conical loaves, prepared by simple fusion of the native sulfid. It is soft, fusible, readily pulverized, and has a bright metallic luster.

Heated in air, it is decomposed into SO_2 and a brown, vitreous, more or less transparent mass, composed of varying proportions of oxid and oxysulfids, known as *crocus*, or *liver*, or *glass of antimony*. Sb_2S_3 is an anhydrid, corresponding to which are salts known as **thioantimonites**, having the general formula $\text{M}'_2\text{HSbS}_3$. If an excess of Sb_2S_3 be boiled with a solution of potash or soda, a liquid is obtained, which contains an alkaline thioantimonite, and an excess of Sb_2S_3 . If this solution be filtered, and decomposed by an acid while still hot, an orange-colored, amorphous precipitate is produced, which is the **antimonium sulfuratum** (U. S.; Br.), and consists of a mixture, in varying proportions, of Sb_2S_3 and Sb_2O_3 . If, however, the solution be allowed to cool, a brown, voluminous, amorphous precipitate separates, which consists of antimony trisulfid and trioxid, potassium or sodium sulfid, and alkaline thioantimonite in varying proportions; and is known as **Kermes mineral**. If now the solution from which the Kermes has been separated, be decomposed with H_2SO_4 a reddish

yellow substance separates, which is the **golden sulfuret of antimony**, and consists of a mixture of Sb_2S_3 and Sb_2S_5 . The precipitate obtained when H_2S acts upon a solution of an antimonial compound is, according to circumstances, Sb_2S_3 or Sb_2S_5 , mixed with free S. By the action of HCl on Sb_2S_3 , H_2S is produced.

Antimony Pentasulfid— Sb_2S_5 —400—is obtained by decomposing an alkaline thioantimonate by an acid. It is a dark orange-red, amorphous powder, readily soluble in solutions of the alkalies, and alkaline sulfids, with which it forms **thioantimonates**.

An oxysulfid, $\text{Sb}_2\text{S}_5\text{O}_3$, is obtained by the action of a solution of sodium thiosulfate upon SbCl_3 or tartar emetic. It is a fine red powder, used as a pigment, and called **antimony cinnabar** or **antimony vermilion**.

Action of Antimony Compounds on the Economy.—The compounds of antimony are poisonous, and act with greater or less energy as they are more or less soluble. The compound which is most frequently the cause of antimonial poisoning is tartar emetic (q. v.), which has caused death in a quantity of three grains, in divided doses, although recovery has followed the ingestion of half an ounce in several instances. Indeed, the chances of recovery seem to be better with large, than with small doses, probably owing to the more rapid and complete removal of the poison by vomiting with large doses. Antimonials have been sometimes criminally administered in small and repeated doses, the victim dying of exhaustion. In such a case an examination of the urine will reveal the cause of the trouble.

If vomiting have not occurred in cases of acute antimonial poisoning it should be provoked by warm water, or the stomach should be washed out. Tannin in some form (decoction of oak bark, cinchona, nutgalls, tea) should then be given, with a view to rendering any remaining poison insoluble.

Medicinal antimonials are very liable to contamination with arsenic.

Analytical Characters of Antimonial Compounds.—(1) With H_2S in acid solution: an orange-red ppt., soluble in NH_4HS and in hot HCl .

(2) A strip of bright copper, suspended in a boiling solution of an Sb compound, acidulated with HCl , is coated with a blue-gray deposit. This deposit when dried (on the copper), and heated in a tube, open at both ends yields a white, *amorphous* sublimate (see No. 5, p. 178).

(3) Antimonial compounds yield a deposit by Marsh's test, similar to that obtained with arsenical compounds, but differing in the particulars given above (see No. 6, p. 181).

IV. BORON GROUP.

BORON.

Symbol=B—*Atomic weight*=11 (O=16.11; H=1.10.91)—*Molecular weight*=22 (1)—*Isolated by Davy in 1807.*

Boron occurs in nature in the borates of Ca, Mg, and Na, principally as sodium pyroborate (borax). It constitutes a group by itself; it is trivalent in all of its compounds; it forms but one oxid, which is the anhydrid of a tribasic acid; and it forms no compound with H.

It is separable in two allotropic modifications. **Amorphous boron** is prepared by decomposition of the oxid, by heating with metallic potassium or sodium. It is a greenish brown powder; sparingly soluble in H₂O; infusible; and capable of direct union with Cl, Br, O, S, and N. **Crystallized boron** is produced when the oxid, chlorid or fluorid is reduced by Al. It crystallizes in quadratic prisms; more or less transparent, and varying in color from a faint yellow to deep garnet-red; very hard; sp. gr. 2.68. It burns when strongly heated in O, and readily in Cl; it also combines with N, which it is capable of removing from NH₃ at a high temperature.

Boron Trioxid.—*Boric or boracic anhydrid*—B₂O₃—70—is obtained by heating boric acid to redness in a platinum vessel. It is a transparent, glass-like mass, used in blowpipe analysis under the name **vitreous boric acid**.

Boric Acids.—**Boric Acid**—*Boracic acid*—*Orthoboric acid*—*Acidum boricum* (U. S.)—H₃BO₃—62—occurs in nature; and is prepared by slowly decomposing a boiling, concentrated solution of borax, with an excess of H₂SO₄, and allowing the acid to crystallize.

It forms brilliant, crystalline plates, unctuous to the touch; odorless; slightly bitter; soluble in 34 parts H₂O at 10° (50° F.); soluble in alcohol. Its solution reddens litmus, but turns turmeric paper brown. When its aqueous solution is distilled, a portion of the acid passes over.

Boric acid readily forms esters with the alcohols. When heated with ethylic alcohol, **ethyl borate** is formed, which burns with a green flame. Heated with glycerol, a soluble, neutral ester is formed, known as **boroglycerid**, and used as an antiseptic.

If H₃BO₃ be heated for some time at 80° (176° F.), it loses H₂O and is converted into **metaboric acid**, HBO₂. If maintained at 100° (212° F.) for several days, it loses a further quantity of H₂O, and is converted into **tetraboric or pyroboric acid**, H₂B₄O₇, whose sodium salt is borax.

V. CARBON GROUP.

CARBON—SILICON.

The elements of this group are bivalent or quadrivalent. The saturated oxid of each is the anhydrid of a dibasic acid. They are both combustible, and each occurs in three allotropic forms.

CARBON.

Symbol=C—*Atomic weight*=12 (O=16:12; H=1:11.9)—*Molecular weight*=24 (?).

Occurrence.—Free in its three allotropic forms: The **diamond** in octahedral crystals; in alluvial sand, clay, sandstone, and conglomerate; **graphite**, in amorphous or imperfectly crystalline forms; **amorphous**, in the different varieties of anthracite and bituminous coal, jet, etc. In combination, it is very widely distributed in the so-called organic substances.

Properties.—**Diamond.**—The crystals of diamond, which is almost pure carbon, are usually colorless or yellowish, but may be blue, green, pink, brown or black. It is the hardest substance known, and the one which refracts light the most strongly. Its index of refraction is 2.47 to 2.75. It is brittle; a bad conductor of heat and of electricity; sp. gr. 3.50 to 3.55. When very strongly heated in air it burns, without blackening, to carbon dioxid.

Graphite is a form of carbon almost as pure as the diamond, capable of crystallizing in hexagonal plates; sp. gr. 2.2; dark gray in color; opaque; soft enough to be scratched by the nail; and a good conductor of electricity. It is also known as **black lead** or **plumbago**. It has been obtained artificially, by allowing molten cast-iron, containing an excess of carbon, to cool slowly, and dissolving the iron in HCl. When oxidized with potassium chlorate and nitric acid it yields **graphitic acid**, $C_{11}H_4O_5$.

Amorphous carbon is met with in a great variety of forms, natural and artificial, in all of which it is black; sp. gr. 1.6–2.0; more or less porous; and a conductor of electricity.

Anthracite coal is hard and dense; it does not flame when burning; is difficult to kindle, but gives great heat with a suitable draught. It contains 80–90 per cent. of carbon. **Bituminous** coal differs from anthracite in that, when burning, it gives off gases, which produce a flame. Some varieties are quite soft, while others, such as jet, are hard enough to assume a high polish. It is usually compact in texture, and very frequently contains impressions of

leaves, and other parts of plants. It contains about 75 per cent. of carbon.

Charcoal, carbo ligni, U. S., is obtained by burning woody fiber, with an insufficient supply of air. It is brittle and sonorous; has the form of the wood from which it was obtained, and retains all the mineral matter present in the woody tissue. Its sp. gr. is about 1.57. It has the power of condensing within its pores odorous substances and large quantities of gases; 90 volumes of ammonia, 55 of hydrogen sulfid, 9.25 of oxygen. This property is taken advantage of in a variety of ways. Its power of absorbing odorous bodies renders it valuable as a disinfecting and filtering agent, and in the prevention of putrefaction and fermentation of certain liquids. The efficacy of charcoal as a filtering material is due also, in a great measure, to the oxidizing action of the oxygen condensed in its pores; indeed, if charcoal be boiled with dilute HCl, dried, and heated to redness, the oxidizing action of the oxygen, which it thus condenses, is very energetic.

When small strips of wood are heated to redness in a current of vapor of carbon disulfid, or of hydrocarbons, **metallic carbon** is produced. This is very sonorous, and is a very good conductor of heat and of electricity. The filaments in incandescent electric lamps are prepared from vegetable parchment or bamboo fiber in a similar manner.

Lamp-black is obtained by incomplete combustion of some resinous or tarry substance, or natural gas, the smoke or soot from which is directed into suitable condensing chambers. It is a light, amorphous powder, and contains a notable quantity of oily and tarry material, from which it may be freed by heating in a covered vessel. It is used in the manufacture of printer's ink.

Coke is the substance remaining in gas retorts, after the distillation of bituminous coal, in the manufacture of illuminating gas. It is a hard, grayish substance, usually very porous, dense, and sonorous. When iron retorts are used, a portion of the gaseous products are decomposed by contact with the hot iron surface, upon which there is then deposited a layer of very hard, compact, grayish carbon, which is a good conductor of electricity.

Animal charcoal is obtained by calcining animal matters in closed vessels. If prepared from bones it is known as **bone-black, carbo animalis**, U. S.; if from ivory, **ivory black**. The latter is used as a pigment, the former as a decolorizing agent. Bones yield about 60 per cent. of bone-black, which contains, besides carbon, nitrogen and the phosphates and other mineral substances of the bones. It possesses in a remarkable degree the power of absorbing coloring matters. When its decolorizing power is lost by saturation with pig-

mentary bodies, it may be restored, although not completely, by calcination. For certain purposes purified animal charcoal, i. e., freed from mineral matter, *carbo animalis purificatus*, U. S., is required, and is obtained by extracting the commercial article with HCl, and washing it thoroughly. Its decolorizing power is diminished by this treatment. Animal charcoal has the power of removing from a solution certain crystalline substances, notably the alkaloids, and a method has been suggested for separating these bodies from organic mixtures by its use.

All forms of carbon are insoluble in any known liquid.

Chemical.—All forms of C combine with O at high temperatures, with light and heat. The product of the union is carbon dioxid if the supply of air or O be sufficient; but if O be present in limited quantity, carbon monoxid is formed. The affinity of C for O renders it a valuable reducing agent. Many metallic oxids are reduced, when heated with C, and steam is decomposed when passed over red-hot C: $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$. At elevated temperatures C also combines directly with S, to form carbon disulfid. With H, carbon also combines directly, under the influence of the voltaic arc.

For Compounds of Carbon, see page 262.

SILICON.

Symbol=Si—*Atomic weight*=28 (O=16:28.4; H=1:28.17)—*Molecular weight*=56 (1)—*Discovered by* Davy, 1807—*Name from* silex=*flint*.

Also known as *silicium*; occurs in three allotropic forms: **Amorphous silicon**, formed when silicon chlorid is passed over heated K or Na, is a dark brown powder, heavier than water. When heated in air, it burns with a bright flame to the dioxid. It dissolves in potash and in hydrofluoric acid, but is not attacked by other acids. **Graphitoid silicon** is obtained by fusing potassium fluosilicate with aluminium. It forms hexagonal plates, of sp. gr. 2.49, which do not burn when heated to whiteness in O, but may be oxidized at that temperature, by a mixture of potassium chlorate and nitrate. It dissolves slowly in alkaline solutions, but not in acids. **Crystallized silicon**, corresponding to the diamond, forms crystalline needles, which are only attacked by a mixture of nitric and hydrofluoric acids.

Silicon, although closely related to C, exists in nature in comparatively few compounds. It has been caused to form artificial combinations, however, which indicate its possible capacity to exist in substances corresponding to those C compounds commonly known as

organic, e. g., **silicichloroform** and **silicibromoform**, SiHCl_3 and SiHBr_3 .

Hydrogen Silicid— SiH_4 —32—is obtained as a colorless, insoluble, spontaneously inflammable gas, by passing the current of a galvanic battery of twelve cells through a solution of common salt, using a plate of aluminium, alloyed with silicon, as the positive electrode.

Silicon Chlorid— SiCl_4 —170—a colorless, volatile liquid, having an irritating odor; sp. gr. 1.52; boils at 59° (138.2°F.); formed when Si is heated to redness in Cl.

Silicic Oxid—*Silicic anhydrid*—*Silex*— SiO_2 —60—is the most important of the compounds of silicon. It exists in nature in the different varieties of quartz, and in the rocks and sands containing that mineral, in agate, carnelian, flint, etc. Its purest native form is **rock crystal**. Its hydrates occur in the opal, and in solution in natural waters. When crystallized, it is fusible with difficulty. When heated to redness with the alkaline carbonates, it forms **silicates**, which solidify to glass-like masses, on cooling. It unites with H_2O to form a number of acid hydrates. The normal hydrate, H_4SiO_4 , has not been isolated, although it probably exists in the solution obtained by adding an excess of HCl to a solution of sodium silicate. A gelatinous hydrate, soluble in water and in acids and alkalis, is obtained by adding a small quantity of HCl to a concentrated solution of sodium silicate.

Hydrofluosilicic Acid— H_2SiF_6 —144—is obtained in solution by passing the gas disengaged by gently heating a mixture of equal parts of fluorspar and pounded glass and 6 pts. H_2SO_4 through water; the disengagement tube being protected from moisture by a layer of mercury. It is used in analysis as a test for K and Na.

Silicon Carbid— SiC —is produced by the action of a powerful electric current upon a mixture of coke and aluminium silicate. It forms blue crystals, is very hard, and is used as a polishing agent under the name **Carborundum**.

VI. VANADIUM GROUP.

VANADIUM—NIOBIUM—TANTALUM.

The elements of this group resemble those of the N group, but are usually quadrivalent.

Vanadium—V—51.2—a brilliant, crystalline metal; sp. gr.=5.5; which forms a series of oxids similar to those of N. No salts of V are known, but salts of vanadyl (VO) are numerous, and are used in the manufacture of anilin black.

Niobium (Columbium)—Nb—94—a bright, steel-gray metal; sp. gr. 7.06; which burns in air to Nb_2O_5 and in Cl to NbCl_5 ; not attacked by acids.

Tantalum—Ta—183—closely resembles Nb in its chemical characters.

VII. MOLYBDENUM GROUP.

MOLYBDENUM—TUNGSTEN—OSMIUM.

The position of this group is doubtful; and it is probable that the lower oxids will be found to be basic in character, in which case the group should be transferred to the third class.

Molybdenum—Mo—96—a brittle white metal. The oxid MoO_3 , *molybdic anhydrid*, combines with H_2O to form a number of acids; the ammonium salt of one of which is used as a reagent for H_3PO_4 ; with which it forms a conjugate acid, *phosphomolybdic acid*, used as a reagent for the alkaloids.

Tungsten—Wolfram—W—184—a hard, brittle metal; sp. gr. 17.4. The oxid, WO_3 , *tungstic anhydrid*, is a yellow powder, forming with H_2O several acid hydrates; one of which, *metatungstic acid*, is used as a test for the alkaloids, as are also the conjugate *silicotungstic* and *phosphotungstic acids*. Tissues impregnated with *sodium tungstate* are rendered uninflamable.

Osmium—Os—191—occurs in combination with Ir in Pt ores; combustible and readily oxidized to OsO_4 . This oxid, known as *osmic acid*, forms colorless crystals, soluble in H_2O , which give off intensely irritating vapors. It is used as a staining agent by histologists, and also in dental practice.

CLASS IV.—AMPHOTERIC ELEMENTS.

Elements whose Oxids unite with Water, some to form Bases, others to form Acids; which form Oxysalts.

The elements of this class are intermediate between the acidulous and the basylous elements, not only in the chemical relations of their oxids, but also in the products of their electrolytic dissociation. While the acidulous elements usually exist in ionized solutions in anions, which may be simple or compound, and the basylous elements exist only in cations, which are always simple, the amphoteric elements may exist in either anion or cation. When they occur in cations the ions are almost always simple, as triaurion, Au^{+++} , diferrion, Fe^{++} , plumbion, Pb^{++} , etc., although rarely they are compound, as diuranion, UO_2^{++} . When they occur in anions these are invariably compound, as dichromanion, $\text{Cr}_2\text{O}_7^{--}$, permanganion, MnO_4^{--} , ferrocyanidion, $\text{Fe}(\text{CN})_6^{--}$, etc.

I. GOLD GROUP.

GOLD.

Symbol = Au (*Aurum*) — *Atomic weight* = 197 ($\text{O} = 16; 197.2; \text{H} = 1; 195.63$) — *Molecular weight* = 394 (?) — *Sp. gr.* = 19.258–19.367 — *Fuses at* 1200° (2192°F.).

Gold forms two series of compounds; in one, AuCl , it is univalent; in the other, AuCl_3 , trivalent. Its hydroxid, auric acid, $\text{Au}(\text{OH})_3$, corresponds to the oxid, Au_2O_3 . Its oxysalts are unstable.

It is yellow or red by reflected light, green by transmitted light, reddish purple when finely divided; not very tenacious; softer than silver; very malleable and ductile. It is not acted on by H_2O or air, at any temperature, nor by any single acid. It combines directly with Cl, Br, I, P, Sb, As and Hg. It dissolves in nitromuriatic acid.

Aurous Chlorid— AuCl —is produced when auric chlorid is heated to 185° (365°F.).

Auric Chlorid—*Gold trichlorid*— AuCl_3 —303.6—obtained by dissolving Au in aqua regia, evaporating at 100° (212°F.), and purifying by crystallization from H_2O . Deliquescent, yellow prisms, very soluble in H_2O , alcohol and ether; readily decomposed, with separation of Au, by contact with P, or with reducing agents. Its solution, treated with the chlorids of tin, deposits a purple double stannate of Sn and Au, called "*purple of Cassius*." With alkaline chlorids and with the chlorids of many organic nitrogenous bases it forms crystalline chloraurates, which are salts of hydrochlorauric acid, HAuCl_4 , such as sodium chloraurate, NaAuCl_4 .

Analytical Characters.—(1) With H_2S , from neutral or acid solution: a blackish brown ppt. in the cold; insoluble in HNO_3 and in HCl ; soluble in aqua regia, and in yellow NH_4HS . (2) With stannous chlorid and a little chlorin water, a purple-red ppt., insoluble in HCl . (3) With ferrous sulfate: a brown deposit, which assumes the luster of gold when dried and burnished.

II. IRON GROUP.

CHROMIUM—MANGANESE—IRON.

The elements of the group form two series of compounds. In one they are bivalent, as in $\text{Fe}''\text{Cl}_2$ or $\text{Mn}''\text{SO}_4$, while in the other they are quadrivalent; but when quadrivalent, the atoms do not enter into combination singly, but grouped, two together, to form a hexavalent

unit $\left[\begin{array}{c} \text{Fe} \equiv \\ | \\ \text{Fe} \equiv \end{array} \right]^{\text{vi}}$, as in $(\text{Fe}_2)^{\text{vi}}\text{Cl}_6$, $(\text{Cr}_2)^{\text{vi}}\text{O}_3$. They form several oxids; of

which the oxid MO_3 is an anhydrid, corresponding to which are acids and salts. Most of the other oxids are basic.

CHROMIUM.

Symbol = Cr — *Atomic weight* = 52 (O=16:52.1; H=1:51.69) — *Molecular weight* = 104.12 (?) — *Sp. gr.* = 6.8 — *Discovered by Vauquelin*, 1797 — *Name from χρῶμα* = color.

Occurs in nature principally as chrome ironstone, a double oxid of Cr and Fe. The element is separated with difficulty by reduction of its oxid by charcoal, or of its chlorid by sodium. It is a hard, crystalline, almost infusible metal. Combines with O only at a red heat. It is not attacked by acids, except HCl ; is readily attacked by alkalis.

Chromic Oxid—*Sesquioxid, or green oxid of chromium*— Cr_2O_3 —152.2—obtained, amorphous, by calcining a mixture of potassium dichromate and starch, or, crystallized, by heating neutral potassium chromate to redness in Cl .

It is green; insoluble in H_2O , acids and alkalies; fusible with difficulty, and not decomposed by heat; not reduced by H. At a red heat in air, it combines with alkaline hydroxids and nitrates, to form chromates. It forms two series of salts, the terms of one of which are green, those of the other violet. The alkaline hydroxids separate a bluish-green hydrate from solutions of the green salts, and a bluish violet hydrate from those of the violet salts.

Chromium green, or **emerald green**, is a green hydrate, formed by decomposing a double borate of chromium and potassium by H_2O . It is used in the arts as a substitute for the arsenical greens, and is non-poisonous.

Chromic Anhydrid—**Acidum chromicum** (U. S.)— Cr_2O_3 —100— is formed by decomposing a solution of potassium dichromate by excess of H_2SO_4 , and crystallizing.

It crystallizes in deliquescent, crimson prisms, very soluble in H_2O and in dilute alcohol. It is a powerful oxidant, capable of igniting strong alcohol.

The true chromic acid has not been isolated, but salts are known which correspond to three acid hydrates: H_2CrO_4 = chromic acid; $\text{H}_2\text{Cr}_2\text{O}_7$ = dichromic acid; and $\text{H}_2\text{Cr}_3\text{O}_{10}$ = trichromic acid.

Chlorids.—Two chlorids and one oxychlorid of chromium are known. Chromous chlorid, CrCl_2 , is a white solid, soluble, with a blue color, in H_2O . Chromic chlorid, $(\text{Cr}_2)\text{Cl}_6$, forms large red crystals, insoluble in H_2O when pure.

Sulfates.—A violet sulfate crystallizes in octahedra, $(\text{Cr})_2(\text{SO}_4)_3 + 15 \text{ Aq}$, and is very soluble in H_2O . At 100° it is converted into a green salt, $(\text{Cr})_2(\text{SO}_4)_3 + 5 \text{ Aq}$, soluble in alcohol; which, at higher temperatures, is converted into the red, insoluble, anhydrous salt. Chromic sulfate forms double sulfates, containing 24 Aq, with the alkaline sulfates. (See Alums.)

Analytical Characters.—**CHROMOUS SALTS.**—(1) Potash: a brown ppt. (2) Ammonium hydroxid: greenish white ppt. (3) Alkaline sulfids: black ppt. (4) Sodium phosphate: blue ppt.

CHROMIC SALTS.—(1) Potash: green ppt.; an excess of precipitant forms a green solution, from which Cr_2O_3 separates on boiling. (2) Ammonium hydroxid: greenish-gray ppt. (3) Ammonium sulfhydrate: greenish ppt.

CHROMATES.—(1) H_2S in acid solution: brownish color, changing to green. (2) Ammonium sulfhydrate: greenish ppt. (3) Barium chlorid: yellowish ppt. (4) Silver nitrate: brownish red ppt., soluble in HNO_3 or NH_4HO . (5) Lead acetate: yellow ppt., soluble in potash, insoluble in acetic acid.

MANGANESE.

Symbol=Mn—**Atomic weight**=55 (O=16.55; H=1.54.56)—**Molecular weight**=110 (†)—**Sp. gr.**=7.138–7.206.

Occurs chiefly in pyrolusite, MnO_2 , hausmanite, Mn_3O_4 , braunite, Mn_2O_3 , and manganite, $\text{Mn}_2\text{O}_3, \text{H}_2\text{O}$. A hard, grayish, brittle metal; fusible with difficulty; obtained by reduction of its oxids by C at a

white heat. It is not readily oxidized by cold, dry air; but is superficially oxidized when heated. It decomposes H_2O , liberating H, and dissolves in dilute acids.

Oxids.—Manganese forms six oxids, or compounds representing them: **Manganous oxid**, MnO ; **manganoso-manganic oxid**, Mn_3O_4 ; **manganic oxid**, Mn_2O_3 ; **permanganic oxid**, MnO_2 , and **permanganic anhydrid**, Mn_2O_7 , are known free. **Manganic anhydrid**, MnO_3 , has not been isolated. MnO and Mn_2O_3 are basic; Mn_3O_4 and MnO_2 are indifferent oxids; and MnO_3 and Mn_2O_7 are anhydrids, corresponding to the **manganates** and **permanganates**.

Permanganic oxid—*Manganese dioxid, or black oxid*—**Mangari oxidum nigrum** (U. S.); **Manganesii ox. nig.** (Br.)— MnO_2 —86—exists in nature as **pyrolusite**, the principal ore of manganese, in steel gray, or brownish black, imperfectly crystalline masses.

At a red heat it loses 12 per cent. of O: $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$; and at a white heat, a further quantity of O is given off: $2\text{Mn}_3\text{O}_4 = 6\text{MnO} + \text{O}_2$. Heated with H_2SO_4 , it gives off O, and forms manganous sulfate: $2\text{MnO}_2 + 2\text{H}_2\text{SO}_4 = 2\text{MnSO}_4 + 2\text{H}_2\text{O} + \text{O}_2$. With HCl it yields manganous chlorid, H_2O and Cl: $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$. It is not acted on by HNO_3 .

Chlorids.—Two chlorids of Mn are known: **manganous chlorid**, MnCl_2 , a pink, deliquescent, soluble salt, occurring, mixed with ferric chlorid, in the waste liquid of the preparation of Cl; and **manganic chlorid**, Mn_2Cl_6 .

Salts of Manganese.—Manganese forms two series of salts: **Manganous salts**, containing Mn'' ; and **manganic salts**, containing $(\text{Mn}_2)^{\text{vi}}$; the former are colorless or pink, and soluble in water; the latter are unstable.

Manganous Sulfate—**Mangani sulfas** (U. S.)— $\text{MnSO}_4 + n\text{Aq}$ — $150 + n18$ —is formed by the action of H_2SO_4 on MnO_2 . Below 6° (42.8° F.) it crystallizes with 7 Aq, and is isomorphous with ferrous sulfate; between 7° – 20° (44.6° – 68° F.) it forms crystals with 5 Aq, and is isomorphous with cupric sulfate; between 20° – 30° (68° – 86° F.) it crystallizes with 4 Aq. It is rose-colored, darker as the proportion of Aq increases, soluble in H_2O , insoluble in alcohol. With the alkaline sulfates it forms double salts, with 6 Aq.

Analytical Characters.—**MANGANOUS.**—(1) Potash: white ppt., turning brown. (2) Alkaline carbonates: white ppts. (3) Ammonium sulfhydrate: flesh-colored ppt., soluble in acids, sparingly soluble in excess of precipitant. (4) Potassium ferrocyanid: faintly reddish white ppt., in neutral solution; soluble in HCl. (5) Potassium cyanid: rose-colored ppt. forming brown solution with excess.

MANGANIC.—(1) H_2S : ppt. of sulfur. (2) Ammonium sulfhydrate: flesh-colored ppt. (3) Potassium ferrocyanid: greenish ppt. (4) Po-

tassium ferricyanid: brown ppt. (5) Potassium cyanid: light brown ppt.

MANGANATES—are green salts, whose solutions are only stable in presence of excess of alkali, and turn brown when diluted and acidulated.

PERMANGANATES—form red solutions, which are decolorized by SO_2 , other reducing agents, and many organic substances.

IRON.

Symbol = Fe (*Ferrum*) — *Atomic weight* = 56 (O = 16:56; H = 1:55.56) — *Molecular weight* = 111.8 (?) — *Sp. gr.* = 7.25–7.9 — *Fuses at* 1600° (2912° F.) — *Name from the Saxon*, *iren*.

Occurrence.—Free, in small quantity only, in platinum ores and meteorites. As Fe_2O_3 in *red hæmatite* and *specular iron*; as hydrates of Fe_2O_3 in *brown hæmatite* and *öölitic iron*; as Fe_3O_4 in *magnetic iron*; as FeCO_3 in *spathic iron*, *clay ironstone* and *bog ore*; and as FeS_2 in *pyrites*. It is also a constituent of most soils and clays, exists in many mineral waters, and in the red blood pigment of animals.

Preparation.—In working the ores, reduction is first effected in a *blast furnace*, into which alternate layers of ore, coal and limestone are fed from the top, while air is forced in from below. In the lower part of the furnace CO_2 is produced, at the expense of the coal; higher up it is reduced by the incandescent fuel to CO, which, at a still higher point, reduces the ore. The fused metal, so liberated, collects at the lowest point, under a layer of *slag*; and is drawn off to be cast as *pig iron*. This product is then purified, by burning out impurities, in the process known as *puddling*.

Pure iron is prepared by reduction of ferrous chlorid, or of ferric oxid, by H at a temperature approaching redness.

Varieties.—*Cast iron* is a brittle, white or gray, crystalline metal, consisting of Fe 89–90%; C 1–4.5%; and Si, P, S, and Mn. As *pig iron*, it is the product of the blast-furnace.

Wrought, or *bar iron*, is a fibrous, tough metal, freed in part from the impurities of cast iron, by *refining* and *puddling*.

Steel is Fe combined with a quantity of C, less than that existing in cast iron, and greater than that in bar iron. It is prepared by *cementation*; which consists in causing bar iron to combine with C; or by the *Bessemer method*; which, as now used, consists in burning the C out of molten cast iron, to which the proper proportion of C is then added in the shape of *spiegel eisen*, an iron rich in Mn and C.

The purest forms of commercial iron are those used in piano-

strings, the teeth of carding machines and electro magnets; known as *soft iron*.

Reduced iron—*Ferrum reductum* (U. S.)—*Fer. redactum* (Br.)—is Fe, more or less mixed with Fe_2O_3 and Fe_3O_4 , obtained by heating Fe_2O_3 in H.

Properties.—*Physical.*—Pure iron is silver white, quite soft; crystallizes in cubes or octahedra. *Wrought iron* is gray, hard, very tenacious, fibrous, quite malleable and ductile, capable of being welded, highly magnetic, but only temporarily so. *Steel* is gray, very hard and brittle if *tempered*, soft and tenacious if not, permanently magnetic.

Chemical.—Iron is not altered by dry air at the ordinary temperature. At a red heat it is oxidized. In damp air it is converted into a hydrate, *iron rust*. *Tinplate* is sheet iron, coated with tin; *galvanized iron* is coated with zinc, to preserve it from the action of damp air.

Iron unites directly with Cl, Br, I, S, N, P, As, and Sb. It dissolves in HCl as ferrous chlorid, while H is liberated. Heated with strong H_2SO_4 , it gives off SO_2 ; with dilute H_2SO_4 , H is given off and ferrous sulfate formed. Dilute HNO_3 dissolves Fe, but the concentrated acid renders it *passive*, when it is not dissolved by either concentrated or dilute HNO_3 , until the passive condition is destroyed by contact with Pt, Ag or Cu, or by heating to 40° (104° F.).

Compounds of Iron.—**Oxids.**—Three oxids of iron exist free: FeO ; Fe_2O_3 ; Fe_3O_4 .

Ferrous Oxid.—*Protoxid of iron*— FeO —72—is formed by heating Fe_2O_3 in CO or CO_2 .

Ferric Oxid.—*Sesquioxid or peroxid of iron*—*Colcothar*—*Jeweler's rouge*—*Venetian red*— Fe_2O_3 —160—occurs in nature (see above), and is formed when ferrous sulfate is strongly heated, as in the manufacture of pyrosulfuric acid. It is a reddish, amorphous solid, is a weak base, and is decomposed at a white heat into O and Fe_3O_4 .

Magnetic Oxid.—*Black oxid*—*Ferri oxidum magneticum* (Br.)— Fe_3O_4 —232—is the *natural loadstone*, and is formed by the action of air, or steam, upon iron at high temperatures. It is probably a compound of ferrous and ferric oxids (FeO , Fe_2O_3), as acids produce with it mixtures of ferrous and ferric salts.

Hydrates.—**Ferrous.**—When a solution of a ferrous salt is decomposed by an alkaline hydroxid, a greenish-white hydroxid, FeH_2O_2 , is deposited; which rapidly absorbs O from the air, with formation of ferric hydroxid.

Ferric.—When an alkali is added to a solution of a ferric salt, a brown, gelatinous precipitate is formed, which is the *normal ferric hydroxid* $(\text{Fe})_2\text{H}_6\text{O}_6$ = *Ferri peroxidum hydratum* (U. S.); *Fer.*

perox. humidum (Br.). It is not formed in the presence of fixed organic acids, or of sugar in sufficient quantity. If preserved under H_2O , it is partly oxidized, forming an oxyhydrate which is incapable of forming ferrous arsenate with As_2O_3 .

If the hydroxid $(Fe_2)H_6O_6$, be dried at 100° (212° F.), it loses $2H_2O$, and is converted into $(Fe_2)O_2, H_2O_2$, which is the *Ferri peroxidum hydratum* (Br.).

If the normal hydroxid be dried *in vacuo*, it is converted into $(Fe_2)_2H_6O_9$, and this, when boiled for some hours with H_2O , is converted into the colloid or modified hydrate $(Fe_2)H_2O_4$ (?), which is brick-red in color, almost insoluble in HNO_3 and HCl , gives no Prussian blue reaction, and forms a turbid solution with acetic acid. If recently precipitated ferric hydroxid be dissolved in solution of ferric chlorid or acetate, and subjected to dialysis, almost all the acid passes out, leaving in the dialyzer a dark red solution, which probably contains this colloid hydrate, and which is instantly coagulated by a trace of H_2SO_4 , by alkalies, many salts, and by heat; dialyzed iron.

Ferric Acid.— H_2FeO_4 .—Neither the free acid nor the oxid, FeO_3 , is known in the free state; the **ferrates**, however, of Na, K, Ba, Sr, and Ca are known.

Sulfids.—**Ferrous Sulfid**—*Protosulfid of iron*— FeS —88—is formed :

(1) By heating a mixture of finely-divided Fe and S to redness; (2) by pressing roll-sulfur on white-hot iron; (3) in a hydrated condition, FeS, H_2O , by treating a solution of a ferrous salt with an alkaline sulfhydrate.

The dry sulfid is a brownish, brittle, magnetic solid, insoluble in H_2O , soluble in acids with evolution of H_2S . The hydrate is a black powder, which absorbs O from the air, turning yellow, by formation of Fe_2O_3 , and liberation of S. It occurs in the fæces of persons taking chalybeate waters or preparations of iron.

Ferric Sulfid—*Sesquisulfid*— Fe_2S_3 —208—occurs in nature in *copper pyrites*, and is formed when the disulfid is heated to redness.

Ferric Disulfid— FeS_2 —120—occurs in the *white and yellow Martial pyrites*, used in the manufacture of H_2SO_4 . When heated in air, it is decomposed into SO_2 and *magnetic pyrites*: $3FeS_2 + 2O_2 = Fe_3S_4 + 2SO_2$.

Chlorids.—**Ferrous Chlorid**—*Protochlorid*— $FeCl_2$ —126.9—is produced: (1) by passing dry HCl over red-hot Fe; (2) by heating ferric chlorid in H; (3) as a hydrate, $FeCl_2, 4H_2O$, by dissolving Fe in HCl .

The anhydrous compound is a yellow, crystalline, volatile, and very soluble solid. The hydrated is in greenish, oblique rhombic

prisms, deliquescent and very soluble in H_2O and alcohol. When heated in air it is converted into ferric chlorid, and an oxy-chlorid.

Ferric Chlorid—Sesquichlorid—Perchlorid—Ferri chloridum (U. S.)— Fe_2Cl_6 —324.7—is produced, in the anhydrous form, by heating Fe in Cl. As a hydrate, $Fe_2Cl_6, 4H_2O$, or $Fe_2Cl_6, 6H_2O$, it is formed: (1) by solution of the anhydrous compound; (2) by dissolving Fe in aqua regia; (3) by dissolving ferric hydroxid in HCl; (4) by the action of Cl or of HNO_3 on solution of ferrous chlorid. It is by the last method that the pharmaceutical product is obtained.

The anhydrous compound forms reddish-violet, crystalline plates, very deliquescent. The hydrates form yellow, nodular, imperfectly crystalline masses, or rhombic plates, very soluble in H_2O , soluble in alcohol and ether. In solution, it is converted into $FeCl_2$ by reducing agents. The **Liq. ferri chloridi** (U. S.)=**Liq. fer. perchloridi** (Br.) is an aqueous solution of this compound, containing excess of acid. The **Tinct. fer. chlor.** (U. S.) and **Tinct. fer. perchl.** (Br.) are the solution, diluted with alcohol, and contain ethyl chlorid and ferrous chlorid.

Bromids.—Ferrous Bromid—FeBr₂—215.9—is formed by the action of Br on excess of Fe, in presence of H_2O .

Ferric Bromid—Fe₂Br₆—591.7—is prepared by the action of excess of Br on Fe.

Iodids.—Ferrous Iodid—Ferri iodidum (U. S.; Br.)— FeI_2 —309.7—is obtained, with $4H_2O$, by the action of I upon excess of Fe in the presence of warm H_2O . When anhydrous, it is a white powder; hydrated, it is in green crystals. In air it is rapidly decomposed, more slowly in the presence of sugar.

Ferric Iodid—Fe₂I₆—873—is formed by the action of excess of I on Fe.

Salts of Iron.—Sulfates.—Ferrous Sulfate—Protosulfate—Green vitriol—Copperas—Ferri sulfas (U. S.; Br.)— $FeSO_4 + 7Aq$ —152 + 126—is formed: (1) by oxidation of the sulfid, Fe_3S_4 , formed in the manufacture of H_2SO_4 ; (2) by dissolving Fe in dilute H_2SO_4 .

It forms green, efflorescent, oblique rhombic prisms, quite soluble in H_2O , insoluble in alcohol. It loses 6 Aq at 100° (212° F.) (**Ferr. sulf. exsiccatus**, U. S.); and the last Aq at about 300° (572° F.). At a red heat it is decomposed into Fe_2O_3 ; SO_2 and SO_3 . By exposure to air it is gradually converted into a basic ferric sulfate, $(Fe_2)(SO_4)_3, 5Fe_2O_3$.

Ferric Sulfates are quite numerous, and are formed by oxidations of ferrous sulfate under different conditions. The normal sulfate, $(Fe_2)(SO_4)_3$, is formed by treating solution of $FeSO_4$ with HNO_3 , and evaporating, after addition of one molecule of H_2SO_4 for each

two molecules of FeSO_4 . The **Liq. fer. tersulfatis** (U. S.), contains this salt. It is a yellowish white, amorphous solid.

Of the many basic ferric sulfates, the only one of medical interest is **Monsel's salt**, $5(\text{Fe}_2)(\text{SO}_4)_3 + 4\text{Fe}_2\text{O}_3$, which exists in the **Liq. ferri subsulfatis** (U. S.) and **Liq. fer. persulfatis** (Br.). Its solution is decolorized, and forms a white deposit with excess of H_2SO_4 .

Nitrates.—**Ferrous Nitrate**— $\text{Fe}(\text{NO}_3)_2$ —179.1—a greenish, unstable salt, formed by double decomposition between barium nitrate and ferrous sulfate; or by the action of HNO_3 on FeS .

Ferric Nitrates.—The *normal nitrate*— $(\text{Fe}_2)(\text{NO}_3)_6$ —484.2—is obtained in solution by dissolving Fe in HNO_3 of sp. gr. 1.115; or by dissolving ferric hydroxid in HNO_3 . It therefore exists in the *Liq. ferri nitratis* (U. S.). It crystallizes in rhombic prisms with 18 Aq, or in cubes with 12 Aq.

Several basic nitrates are known, all of which are uncrystallizable, and by their presence (as when Fe is dissolved in HNO_3 to saturation) prevent the crystallization of the normal salt.

Phosphates.—**Triferrous Phosphate**— $\text{Fe}_3(\text{PO}_4)_2$ —358.—A white precipitate, formed by adding disodic phosphate to a solution of a ferrous salt, in presence of sodium acetate. By exposure to air it turns blue; a part being converted into ferric phosphate. The *ferri phosphas* (Br.) is such a mixture of the two salts. It is insoluble in H_2O ; sparingly soluble in H_2O containing carbonic or acetic acid.

It is probably this phosphate, capable of turning blue, which sometimes occurs in the lungs in phthisis, in blue pus, and in long-buried bones.

Ferric Phosphate— $(\text{Fe}_2)(\text{PO}_4)_2$ —302—is produced by the action of an alkaline phosphate on ferric chlorid. It is soluble in HCl , HNO_3 , citric and tartaric acids, insoluble in phosphoric acid and in solution of disodic phosphate. The *ferri phosphas* (U. S.) is a compound, or mixture of this salt with disodic citrate, which is soluble in water.

There exist quite a number of basic ferric phosphates.

Ferric Pyrophosphate— $(\text{Fe}_2)_2(\text{P}_2\text{O}_7)_3$ —746—is precipitated by decomposition of a solution of a ferric compound by sodium pyrophosphate; an excess of the Na salt dissolves the precipitate when warmed, and, on evaporation, leaves the scales of a double salt, $(\text{Fe}_2)_2(\text{P}_2\text{O}_7)_3, \text{Na}_8(\text{P}_2\text{O}_7)_2 + 20 \text{ Aq}$.

The *ferri pyrophosphas* (U. S.) is a mixture of ferric pyrophosphate, trisodic citrate, and ferric citrate.

Acetates.—**Ferrous Acetate**— $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$ —174—is formed by decomposition of ferrous sulfate by calcium acetate, in soluble, silky needles.

Ferric Acetates.—The *normal salt* $(\text{Fe}_2)(\text{C}_2\text{H}_3\text{O}_2)_6$, is obtained by adding slight excess of ferric sulfate to lead acetate, and decanting after twenty-four hours. It is dark-red, uncrystallizable, very soluble in alcohol, and in H_2O . If its solution be heated it darkens suddenly, gives off acetic acid, and contains a basic acetate. When boiled, it loses all its acetic acid, and deposits ferric hydrate. When heated in closed vessels to 100° (212°F.), and treated with a trace of mineral acid, it deposits the modified ferric hydrate.

Ferrous Carbonate— FeCO_3 —*Spathic iron—clay ironstone—bog ore*—116—occurs as an ore of iron, and is obtained, in a hydrated form, by adding an alkaline carbonate to a ferrous salt. It is a greenish, amorphous powder, which on exposure to air turns red by formation of ferric hydrate; a change which is retarded by the presence of sugar, hence the addition of that substance in the *ferri carbonas saccharatus* (U. S.; Br.). It is insoluble in pure H_2O , but soluble in H_2O containing carbonic acid, probably as *ferrous bicarbonate*, $\text{H}_2\text{Fe}(\text{CO}_3)_2$, in which form it occurs in chalybeate waters.

Ferrous Lactate—*Ferri lactas* (U. S.)— $\text{Fe}(\text{C}_3\text{H}_5\text{O}_3)_2 + 3 \text{Aq}$ —234+54—is formed when iron filings are dissolved in lactic acid. It crystallizes in greenish yellow needles; soluble in H_2O ; insoluble in alcohol; permanent in air when dry.

Ferrous Oxalate—*Ferri oxalas* (U. S.) $\text{FeC}_2\text{O}_4 + 2 \text{Aq}$ —144+36—is a yellow, crystalline powder; sparingly soluble in H_2O ; formed by dissolving iron filings in solution of oxalic acid.

Tartrates—**Ferrous Tartrate**— $\text{FeC}_4\text{H}_4\text{O}_6 + 2 \text{Aq}$ —204+36.—A white, crystalline powder; formed by dissolving Fe in hot concentrated solution of tartaric acid.

Ferric Tartrate— $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_3 + 3 \text{Aq}$ —556+54.—A dirty yellow, amorphous mass, obtained by dissolving recently precipitated ferric hydroxid in tartaric acid solution, and evaporating below 59° (122°F.).

A number of double tartrates, containing the group $(\text{Fe}_2\text{O}_2)''$ are also known. Such are: **Ferrico-ammonic tartrate**=*ferri et ammonii tartras* (U. S.), $(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Fe}_2\text{O}_2)(\text{NH}_4)_2 + 4 \text{Aq}$, and **Ferrico-potassic tartrate**=*ferri et potassii tartras* (U. S.), $(\text{C}_4\text{H}_4\text{O}_6)_2(\text{Fe}_2\text{O}_2)\text{K}_2$. They are prepared by dissolving recently precipitated ferric hydroxid in hot solutions of the hydro-alkaline tartrate. They only react with ferrocyanids and thiocyanates after addition of a mineral acid.

Citrates.—**Ferric Citrate**—*Ferri citras* (U. S.)— $(\text{Fe}_2)(\text{C}_6\text{H}_5\text{O}_7)_2 + 6 \text{Aq}$ —490+108—is in garnet-colored scales, obtained by dissolving ferric hydrate in solution of citric acid, and evaporating the solution at about 60° (140°F.). It loses 3Aq at 120° (248°F.), and the remainder at 150° (302°F.). If a small quantity of ammonium hydroxid be added, before the evaporation, the product consists of

the modified citrate=*ferri et ammonii citras* (U. S.), which only reacts with potassium ferrocyanid after addition of HCl.

The various citrates of iron and alkaloids are not definite compounds.

Ferric Ferrocyanid—Prussian blue— $(\text{Fe}_2)_2(\text{FeC}_6\text{N}_6)_3 + 18\text{Aq}$ —860+324—is a dark-blue precipitate, formed when potassium ferrocyanid is added to a ferric salt. It is insoluble in H_2O , alcohol and dilute acids; soluble in oxalic acid solution (blue ink). Alkalies turn it brown.

Ferrous Ferricyanid—Turnbull's blue— $\text{Fe}_3(\text{Fe}_2\text{C}_{12}\text{N}_{12}) + n\text{Aq}$ —592+n18—is a dark blue substance produced by the action of potassium ferricyanid on ferrous salts. Heated in air it is converted into Prussian blue and ferric oxid.

Analytical Characters.—FERROUS—Are acid; colorless when anhydrous, pale green when hydrated; oxidized by air to basic ferric compounds. (1) Potash: greenish white ppt.; insoluble in excess; changing to green or brown in air. (2) Ammonium hydroxid; greenish ppt.; soluble in excess; not formed in presence of ammoniacal salts. (3) Ammonium sulfhydrate: black ppt.; insoluble in excess; soluble in acids. (4) Potassium ferrocyanid (in absence of ferric salts): white ppt.; turning blue in air. (5) Potassium ferri-cyanid: blue ppt.; soluble in KHO; insoluble in HCl.

FERRIC—Are acid, and yellow or brown. (1) Potash, or ammonium hydroxid: voluminous, red-brown ppt.; insoluble in excess. (2) Hydrogen sulfid, in acid-solution: milky ppt. of sulfur; ferric reduced to ferrous compound. (3) Ammonium sulfhydrate: black ppt.; insoluble in excess; soluble in acids. (4) Potassium ferrocyanid: dark blue ppt.; insoluble in HCl; soluble in KHO. (5) Potassium thiocyanate: dark-red color; prevented by tartaric or citric acid; discharged by mercuric chlorid. (6) Tannin: blue-black color.

III. URANIUM GROUP.

URANIUM.

Symbol=Ur—*Atomic weight*=239.5 (O=16:239.5; H=1:237.6)
—*Sp. gr.*=18.4—*Discovered by Klaproth* (1789).

This element is usually classed with Fe and Cr, or with Ni and Co. It does not, however, form compounds resembling the ferric; it forms a series of well-defined *uranates*, and a series of compounds of the radical *uranyl* (UO)'. Standard solutions of its acetate or nitrate are used for the quantitative determination of H_3PO_4 .

IV. LEAD GROUP.

LEAD.

Symbol = Pb (*Plumbum*)—*Atomic weight* = 207 (O = 16:206.9; H = 1:205.06)—*Molecular weight* = 414 (?)—*Sp. gr.* = 11.445—*Fuses at* 325° (617° F.)—*Name from* læd = heavy (*Saxon*).

Lead is usually classed with Cd, Bi, or Cu and Hg. It differs, however, from Bi in being bivalent or quadrivalent, but not trivalent, and in forming no compounds resembling those of bismuthyl (BiO); from Cd, in the nature of its O compounds; and from Cu and Hg in forming no compounds similar to the mercurous and cuprous salts. Indeed, the nature of the Pb compounds is such that the element is best classed in a group by itself, which finds a place in this class by virtue of the existence of potassium plumbate.

Occurrence.—Its most abundant ore is **galena**, PbS. It also occurs in **white lead ore**, PbCO₃, in **anglesite**, PbSO₄, and in **horn lead**, PbCl₂.

Preparation.—Galena is first roasted with a little lime. The mixture of PbO, PbS, and PbSO₄ obtained is strongly heated in a reverberatory furnace, when SO₂ is driven off. The impure *work lead*, so formed, is purified by fusion in air, and removal of the film of oxids of Sn and Sb. If the ore be rich in Ag, that metal is extracted, by taking advantage of the greater fusibility of an alloy of Pb and Ag, than of Pb alone; and subsequent oxidation of the remaining Pb.

Properties.—*Physical.*—It is a bluish white metal; brilliant upon freshly cut surfaces; very soft and pliable; not very malleable or ductile; crystallizes in octahedra; a poor conductor of electricity; a better conductor of heat. When expanded by heat it does not, on cooling, return to its original volume.

Chemical.—When exposed to air it is oxidized, more readily and completely at high temperatures. The action of H₂O on Pb varies with the conditions. Pure unaërated H₂O has no action upon it. By the combined action of air and moisture Pb is oxidized, and the oxid dissolved in the H₂O, leaving a metallic surface for the continuance of the action. The solvent action of H₂O upon Pb is increased, owing to the formation of basic salts, by the presence of nitrogenized organic substances, nitrates, nitrites, and chlorids. On the other hand, carbonates, sulfates, and phosphates, by their tendency to form insoluble coatings, diminish the corroding action of H₂O. Carbonic acid in small quantity, especially in presence of carbonates, tends to preserve Pb from solution, while H₂O highly charged with it (soda water) dissolves the metal readily. Lead is dissolved, as a nitrate, by HNO₃.

H_2SO_4 , when cold and moderately concentrated, does not affect it; but, when heated, dissolves it the more readily as the acid is more concentrated. It is attacked by HCl of sp. gr. 1.12, especially if heated. Acetic acid dissolves it as acetate, or, in the presence of CO_2 , converts it into white lead.

Oxids.—**Lead Monoxid**—*Protoxid*—**Massicot**—**Litharge**—**Plumbi oxidum** (U. S.; Br.)— PbO —222.9—is prepared by heating Pb , or its carbonate, or nitrate, in air. If the product have been fused, it is **litharge**; if not, **massicot**. It forms copper-colored, mica-like plates, or a yellow powder; or crystallizes, from its solution in soda or potash, in white, rhombic dodecahedra, or in rose-colored cubes. It fuses near a red heat, and volatilizes at a white heat; sp. gr. 9.277–9.5. It is sparingly soluble in H_2O , forming an alkaline solution.

Heated in air to 300° (572° F.) it is oxidized to **minium**. It is readily reduced by H or C . With Cl it forms PbCl_2 and O . It is a strong base; decomposes alkaline salts, with liberation of the alkali. It dissolves in HNO_3 , and in hot acetic acid, as nitrate or acetate. When ground up with oils it saponifies the glycerol ethers, the Pb combining with the fatty acids to form Pb soaps, one of which, **lead oleate**, is the **emplastrum plumbi** (U. S.; Br.). It also combines with the alkalies and earths to form **plumbites**. **Calcium plumbite**, CaPb_2O_3 , is a crystalline salt, formed by heating PbO with milk of lime, and used in solution as a hair dye.

Plumboso-plumbic Oxid—*Red oxid*—**Minium**—**Red lead**— Pb_3O_4 —684.7—is prepared by heating massicot to 300° (572° F.) in air. It ordinarily has the composition Pb_3O_4 , and has been considered as composed of PbO_2 , 2PbO ; or as a basic lead salt of plumbic acid, PbO_3Pb , PbO . An orange-colored variety is formed when lead carbonate is heated to 300° (572° F.).

It is a bright red powder, sp. gr. 8.62. It is converted into PbO when strongly heated, or by the action of reducing agents. HNO_3 changes its color to brown, dissolving PbO and leaving PbO_2 . It is decomposed by HCl , with formation of PbCl_2 , H_2O and Cl .

Lead Dioxid.—*Peroxid*, or *puce oxid*, or *brown oxid*, or *binoxid of lead*—**Plumbic anhydrid**— PbO_2 —238.9—is prepared, either by dissolving the PbO out of red lead by dilute HNO_3 , or by passing a current of Cl through H_2O , holding lead carbonate in suspension.

It is a dark, reddish brown, amorphous powder; sp. gr. 8.903–9.190; insoluble in H_2O . Heated, it loses half its O , and is converted into PbO . It is a valuable oxidant. It absorbs SO_2 to form PbSO_4 . It combines with alkalies to form **plumbates**, M_2PbO_3 .

Plumbic Acid.— H_2PbO_3 —256.9—forms crystalline plates, at the $+$ electrode, when alkaline solutions of the Pb salts are decomposed by a weak current.

Lead Sulfid—Galena— PbS —238.9—exists in nature. It is also formed by direct union of Pb and S; by heating PbO with S, or vapor of CS_2 ; or by decomposing a solution of a Pb salt by H_2S or an alkaline sulfid.

The native sulfid is a bluish gray, and has a metallic luster; sp. gr. 7.58; that formed by precipitation is a black powder; sp. gr. 6.924. It fuses at a red heat and is partly sublimed, partly converted into a subsulfate. Heated in air it is converted into PbSO_4 , PbO and SO_2 . Heated in H it is reduced. Hot HNO_3 oxidizes it to PbSO_4 . Hot HCl converts it into PbCl_2 . Boiling H_2SO_4 converts it into PbSO_4 and SO_2 .

Lead Chlorid— PbCl_2 —277.9—is formed by the action of Cl upon Pb at a red heat; by the action of boiling HCl upon Pb, and by double decomposition between a lead salt and a chlorid.

It crystallizes in plates, or hexagonal needles; sparingly soluble in cold H_2O , less soluble in H_2O containing HCl ; more soluble in hot H_2O , and in concentrated HCl .

Several oxychlorids are known. Cassel, Paris, Verona, or Turner's yellow is PbCl_2 , 7PbO .

Lead Iodid—Plumbi iodidum (U. S.; Br.)— PbI_2 —460.09—is deposited, as a bright yellow powder, when a solution of potassium iodid is added to a solution of Pb salt. Fused in air, it is converted into an oxyiodid. Light and moisture decompose it, with liberation of I. It is almost insoluble in H_2O , soluble in solutions of ammonium chlorid, sodium hyposulfite, alkaline iodids, and potash.

Salts of Lead.—Nitrates.—Lead Nitrate—Plumbi nitras (U. S.; Br.)— $\text{Pb}(\text{NO}_3)_2$ —330.9—is formed by solution of Pb, or of its oxids, in excess of HNO_3 . It forms anhydrous crystals; soluble in H_2O . Heated, it is decomposed into PbO , O and NO_2 .

Besides the neutral nitrate, basic lead nitrates are known, which seem to indicate the existence of nitrogen acids similar to those of phosphorus; $\text{Pb}_3(\text{NO}_4)_2$ —**orthonitrate**; and $\text{Pb}_2\text{N}_2\text{O}_7$ —**pyronitrate**.

Lead Sulfate— PbSO_4 —302.9—is formed by the action of hot, concentrated H_2SO_4 on Pb; or by double decomposition between a sulfate and a Pb salt in solution. It is a white powder, almost insoluble in H_2O , soluble in concentrated H_2SO_4 , from which it is deposited by dilution.

Lead Chromate—Chrome yellow— PbCrO_4 —323.3—is formed by decomposing $\text{Pb}(\text{NO}_3)_2$ with potassium chromate. It is a yellow, amorphous powder, insoluble in H_2O , soluble in alkalis.

Acetates.—Neutral Lead Acetate—Salt of Saturn—Sugar of Lead—Plumbi acetas (U. S.; Br.)— $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{Aq}$ —324.9 + 54—is formed by dissolving PbO in acetic acid; or by exposing Pb in contact with acetic acid to air.

It crystallizes in large, oblique rhombic prisms, sweetish, with a

metallic after-taste; soluble in H_2O and alcohol; its solutions being acid. In air it effloresces, and is superficially converted into carbonate. It fuses at 75.5° (167.9° F.); loses Aq and a part of its acid at 100° (212° F.), forming the sesquibasic acetate, $2[Pb-(C_2H_3O_2)_2]Pb(OH)_2$; at 280° (536° F.) it enters into true fusion, and, at a slightly higher temperature, is decomposed into CO_2 ; Pb, and acetone. Its aqueous solution dissolves PbO, with formation of basic acetates.

Sesquibasic Lead Acetate— $Pb(C_2H_3O_2)OH$, $2PbO$ —728.7—is the main constituent of **Goulard's extract**=**Liq. plumbi subacetatis** (U. S.; Br.), and is formed by boiling a solution of the neutral acetate with PbO in fine powder. The solution becomes milky on addition of ordinary H_2O , from formation of the sulfate and carbonate.

Lead Carbonate— $PbCO_3$ —266.9—occurs in nature as **cerusite**; and is formed, as a white, insoluble powder, when a solution of a Pb compound is decomposed by an alkaline carbonate, or by passing CO_2 through a solution containing Pb.

The **plumbi carbonas** (U. S.; Br.), or **white lead** or **ceruse**, is a basic carbonate $(PbCO_3)_2$, PbH_2O_2 —774.7—mixed with varying proportions of other basic carbonates. It is usually prepared by the action of CO_2 on a solution of the subacetate, prepared by the action of acetic acid on Pb and PbO. It is a heavy, white powder, insoluble in H_2O , except in the presence of CO_2 ; soluble in acids with effervescence; and decomposed by heat into CO_2 and PbO. White lead enters into the composition of almost all oil-paints, being used to dilute other pigments. The darkening of oil-paintings is due to the formation of the black lead sulfid by atmospheric H_2S .

Analytical Characters.—(1) Hydrogen sulfid, in acid solution: a black ppt.; insoluble in alkaline sulfids, and in cold, dilute acids. (2) Ammonium sulfhydrate: black ppt.; insoluble in excess. (3) Hydrochloric acid: white ppt., in not too dilute solution; soluble in boiling H_2O . (4) Ammonium hydroxid: white ppt.; insoluble in excess. (5) Potash: white ppt.; soluble in excess, especially when heated. (6) Sulfuric acid: white ppt.; insoluble in weak acids, soluble in solution of ammonium tartrate. (7) Potassium iodid: yellow ppt.; sparingly soluble in boiling H_2O ; soluble in large excess. (8) Potassium chromate: yellow ppt.; soluble in KHO solution. (9) Iron or zinc separate the element from solution of its salts.

Action on the Economy.—All the soluble compounds of Pb, and those which, although not soluble, are readily convertible into soluble compounds by H_2O , air, or the digestive fluids, are actively poisonous. Some are also injurious by their local action upon tissues with which they come in contact; such are the acetate, and, in less degree, the nitrate.

The **chronic** form of lead intoxication, **painter's colic**, etc., is purely poisonous, and is produced by the continued absorption of minute quantities of Pb, either by the skin, lungs, or stomach. The **acute** form presents symptoms referable to the local, as well as to the poisonous, action of the Pb salt, and is usually caused by the ingestion of a single dose of the acetate or carbonate.

Metallic Pb, although probably not poisonous of itself, causes chronic lead-poisoning by the readiness with which it is convertible into compounds capable of absorption. The principal sources of poisoning by metallic Pb are: the contamination of drinking water which has been in contact with the metal (see p. 119); the use of articles of food, or of chewing tobacco, which has been packed in tin-foil, containing an excess of Pb; the drinking of beer or other beverages which have been in contact with pewter; or the handling of the metal and its alloys.

Almost all the compounds of Pb may produce painter's colic. The carbonate, in painters, artists, manufacturers of white lead, and in persons sleeping in newly-painted rooms; the oxids, in the manufactures of glass, pottery, sealing-wax, and litharge, and by the use of lead-glazed pottery; by other compounds, by the inhalation of the dust of cloth factories, and by the use of lead hair-dyes.

Acute lead-poisoning is of by no means as common occurrence as the chronic form, and usually terminates in recovery. It is caused by the ingestion of a single large dose of the acetate, subacetate, carbonate, or of red lead. In such cases the administration of magnesium sulfate is indicated; it enters into double decomposition with Pb salt to form the insoluble PbSO_4 .

Lead, once absorbed, is eliminated very slowly, it becoming fixed by combination with the proteins, a form of combination which is rendered soluble by potassium iodid. The channels of elimination are by the perspiration, urine and bile.

In the analysis for mineral poisons the major part of the Pb is precipitated as PbS in the treatment by H_2S . The PbS remains upon the filter after extraction with ammonium sulfhydrate. It is treated with warm HCl , which decolorizes it by transforming the sulfid into chlorid. The PbCl_2 thus formed is dissolved in hot H_2O , from which it crystallizes on cooling. The solution still contains PbCl_2 in sufficient quantity to respond to the tests for the metal.

Although Pb is not a normal constituent of the body, the everyday methods by which it may be introduced into the economy, and the slowness of its elimination, are such as to render the greatest caution necessary in drawing conclusions from the detection of Pb in the body after death.

V. BISMUTH GROUP.

BISMUTH.

Symbol=Bi—*Atomic weight*=208.5 (O=16:208.5; H=1:206.8)—*Molecular weight*=420 (?) —*Sp. gr.*=9.677-9.935—*Fuses at* 268° (514.4° F.).

This element is usually classed with Sb; by some writers among the metals, by others in the phosphorus group. We are led to class Bi in our third class, and in a group alone, because: (1) while the so-called salts of Sb are not salts of the element, but of the radical (SbO)', *antimonyl*, Bi enters into saline combination, not only in the radical *bismuthyl* (BiO)', but also as an element; (2) while the compounds of the elements of the N group in which those elements are quinquivalent are, as a rule, more stable than those in which they are trivalent, Bi is trivalent in all its known compounds except one, which is very unstable, in which it is quinquivalent; (3) the hydrates of the N group are strongly acid, and their corresponding salts are stable and well defined; but those hydrates of Bi which are acid are but feebly so, and the bismuthates are unstable; (4) no compound of Bi and H is known.

Occurrence.—Occurs principally free, also as Bi_2O_3 and Bi_2S_3 .

Properties.—Crystallizes in brilliant, metallic rhombohedra; hard and brittle.

It is only superficially oxidized in cold air. Heated to redness in air, it becomes coated with a yellow film of oxid. In H_2O , containing CO_2 , it forms a crystalline subcarbonate. It combines directly with Cl, Br and I. It dissolves in hot H_2SO_4 as sulfate, and in HNO_3 as nitrate.

It is usually contaminated with As, from which it is best purified by heating to redness a mixture of powdered bismuth, potassium carbonate, soap and charcoal, under a layer of charcoal. After an hour the mass is cooled; the button is separated and fused until its surface begins to be coated with a yellowish brown oxid.

Oxids.—Four oxids are known: Bi_2O_2 , Bi_2O_3 , Bi_2O_4 , and Bi_2O_5 .

Bismuth Trioxid—*Bismuthous oxid*—*Protoxid*— Bi_2O_3 —465—is formed by heating Bi, or its nitrate, carbonate or hydrate. It is a pale yellow, insoluble powder; sp. gr. 8.2; fuses at a red heat; soluble in HCl , HNO_3 and H_2SO_4 and in fused potash.

Hydrates.—Bismuth forms at least four hydrates.

Bismuthous Hydroxid— BiH_3O_3 —259.5—is formed, as a white precipitate, when potash or ammonium hydroxid is added to a cold

solution of a Bi salt. When dried it loses H_2O , and is converted into **Bismuthyl hydroxid** $(\text{BiO})\text{HO}$.

Bismuthic acid— $(\text{BiO}_2)\text{HO}$ —257.5—is deposited, as a red powder, when Cl is passed through a boiling solution of potash, holding bismuthous hydroxid in suspension. When heated it is converted into the **pentoxid**, Bi_2O_5 .

Pyrobismuthic Acid— $\text{H}_4\text{Bi}_2\text{O}_7$ —533—is a dark brown powder, precipitated from solution of bismuth nitrate by potassium cyanid.

Bismuth Trichlorid—*Bismuthous chlorid*— BiCl_3 —314.9—is formed by heating Bi in Cl; by distilling a mixture of Bi and mercuric chlorid; or by distilling a solution of Bi in aqua regia. It is a fusible, volatile, deliquescent solid; soluble in dilute HCl. On contact with H_2O it is decomposed with formation of **bismuthyl chlorid**, $(\text{BiO})\text{Cl}$, or **pearl white**.

Bismuth Nitrate— $\text{Bi}(\text{NO}_3)_3 + 5 \text{ Aq}$ —394.5+90—obtained by dissolving Bi in HNO_3 . It crystallizes in large, colorless prisms; at 150° (302° F.), or by contact with H_2O , it is converted into bismuthyl nitrate; at 260° (500° F.) into Bi_2O_3 .

Bismuthyl Nitrate—*Trisnitrate or subnitrate of bismuth*—*Flake white*—**Bismuthi subnitrates**—(U. S.; Br.)— $(\text{BiO})\text{NO}_3\text{H}_2\text{O}$ —304.5—is formed by decomposing a solution of $\text{Bi}(\text{NO}_3)_3$ with a large quantity of H_2O . It is a white, heavy, faintly acid powder; soluble to a slight extent in H_2O when freshly precipitated, the solution depositing it again on standing. It is decomposed by pure H_2O , but not by H_2O containing $\frac{1}{500}$ ammonium nitrate. It usually contains 1 Aq, which it loses at 100° (212° F.) Bismuth subnitrate, as well as the subcarbonate, is liable to contamination with arsenic, which accompanies bismuth in its ores.

Bismuthyl Carbonate—**Bismuth subcarbonate**—**Bismuthi subcarbonas** (U. S.) **Bismuthi carbonas** (Br.)— $(\text{BiO})_2\text{CO}_3\text{H}_2\text{O}$ —527—is a white or yellowish, amorphous powder, formed when a solution of an alkaline carbonate is added to a solution of $\text{Bi}(\text{NO}_3)_3$. It is odorless, tasteless, and insoluble in H_2O and in alcohol.

When heated to 100° (212° F.), it loses H_2O , and is converted into $(\text{BiO})_2\text{CO}_3$. At a higher temperature it is further decomposed into Bi_2O_3 and CO_2 .

Analytical Characters.—(1) Water: white ppt., even in presence of tartaric acid, but not of HNO_3 , HCl, or H_2SO_4 . (2) Hydrogen sulfid: black ppt., insoluble in dilute acids and in alkaline sulfids. (3) Ammonium sulfhydrate: black ppt., insoluble in excess. (4) Potash soda, or ammonia: white ppt., insoluble in excess, and in tartaric acid; turns yellow when the liquid is boiled. (5) Potassium ferrocyanid: yellowish ppt., insoluble in HCl. (6) Potassium ferricyanid: yellowish ppt., soluble in HCl. (7) Infusion of galls:

orange ppt. (8) Potassium iodid: brown ppt., soluble in excess. (9) Reacts with Reinsch's test (*q. v.*), but gives no sublimate in the glass tube.

Action on the Economy.—Although the medicinal compounds of bismuth are probably poisonous, if taken in sufficient quantity, the ill effects ascribed to them are in most, if not all cases, referable to contamination with arsenic. Symptoms of arsenical poisoning have been frequently observed when the subnitrate has been taken internally, and also when it has been used as a cosmetic. Bismuth subnitrate is frequently administered by physicians in cases of arsenical poisoning, not recognized as such during life.

When preparations of bismuth are administered, the alvine discharges contain bismuth sulfid, as a dark brown powder.

VI. TIN GROUP.

TITANIUM—ZIRCONIUM—TIN.

Ti and Sn are bivalent in one series of compounds, SnCl_2 , and quadrivalent in another, SnCl_4 . Zr, so far as known, is always quadrivalent. Each of these elements forms an acid (or salts corresponding to one) of the composition of H_2MO_3 , and a series of oxy-salts of the composition of $\text{M}^{\text{IV}}(\text{NO}_3)_4$.

TITANIUM.

Symbol=Ti—*Atomic weight*=48—*Sp. gr.*=5.3.

Occurs in clays and iron ores, and as TiO_2 in several minerals. Titanic anhydrid, TiO_2 , is a white, insoluble, infusible powder, used in the manufacture of artificial teeth; dissolves in fused KHO, as potassium titanate. Titanium combines readily with N, which it absorbs from air when heated. When NH_3 is passed over red-hot TiO_2 , it is decomposed with formation of the violet nitrid, TiN_2 . Another compound of Ti and N forms hard, copper-colored, cubical crystals.

ZIRCONIUM.

Symbol=Zr—*Atomic weight*=89—*Sp. gr.*=4.15.

Occurs in zircon and hyacinth. Its oxid, zirconia, ZrO_2 , is a white powder, insoluble in KHO. Being infusible, and not altered by exposure to air, it is used in pencils to replace lime in the calcium light.

TIN.

Symbol = Sn (*Stannum*) — *Atomic weight* = 118.5 (O = 16:118.5; H = 1:117.55) — *Molecular weight* = 235.4 (?) — *Sp. gr.* = 7.285–7.293 — *Fuses at* 228° (442.4° F.).

Occurrence.—As **tinestone** (SnO_2) or **cassiterite**, and in **stream tin**.

Preparation.—The commercial metal is prepared by roasting the ore, extracting with H_2O , reducing the residue by heating with charcoal, and refining.

Pure tin is obtained by dissolving the metal in HCl ; filtering; evaporating; dissolving the residue in H_2O : decomposing with ammonium carbonate; and reducing the oxid with charcoal.

Properties.—A soft, malleable, bluish white metal; but slightly tenacious; emits a peculiar sound, the **tin-cry**, when bent. A good conductor of heat and electricity. Air affects it but little, except when it is heated; more rapidly if Sn be alloyed with Pb. It oxidizes slowly in H_2O ; more rapidly in the presence of sodium chlorid. Its presence with Pb accelerates the action of H_2O upon the latter. It dissolves in HCl as SnCl_2 . In presence of a small quantity of H_2O , HNO_3 converts it into metastannic acid. Alkaline solutions dissolve it as metastannates. It combines directly with Cl, Br, I, S, P and As.

Tin plates are thin sheets of Fe, coated with Sn. **Tin foil** consists of thin laminæ of Sn, frequently alloyed with Pb. Copper and iron vessels are **tinned** after brightening, by contact with molten Sn. Pewter, bronze, bell metal, gun metal, britannia metal, speculum metal, type metal, solder, and fusible metal, contain Sn.

Oxids.—**Stannous Oxid**—*Protoxid*— SnO —134.5—obtained by heating the hydroxid or oxalate without contact of air. It is a white, amorphous powder, soluble in acids, and in hot, concentrated solution of potash. It absorbs O readily.

Stannic Oxid—*Binoxid of tin*— SnO_2 —150.5—occurs native as **tinestone** or **cassiterite**, and is formed when Sn or SnO is heated in air. It is used as a polishing material, under the name of **putty powder**.

Hydrates.—**Stannous Hydroxid**— SnH_2O_2 —152.5—is a white precipitate, formed by alkaline hydroxids and carbonates in solutions of SnCl_2 .

Stannic Acid— H_2SnO_3 —168.5—is formed by the action of alkaline hydroxids on solutions of SnCl_4 . It dissolves in solutions of the alkaline hydroxids, forming **stannates**.

Metastannic Acid— $\text{H}_2\text{Sn}_5\text{O}_{11}$ —770.5—is a white, insoluble powder, formed by acting on Sn with HNO_3 .

Chlorids.—**Stannous Chlorid**—*Protochlorid*—**Tin crystals**— $\text{SnCl}_2 + 2\text{Aq}$ —189.4+36—is obtained by dissolving Sn in HCl . It

crystallizes in colorless prisms; soluble in a small quantity of H_2O ; decomposed by a large quantity, unless in the presence of free HCl , with formation of an oxychlorid. Loses its Aq at 100° (212°F.). In air it is transformed into stannic chlorid and oxychlorid. Oxidizing and chlorinating agents convert it into SnCl_4 . It is a strong reducing agent.

Stannic Chlorid—*Bichlorid*—*Liquid of Libavius*— SnCl_4 —260.3—is formed by acting on Sn or SnCl_2 with Cl , or by heating Sn in aqua regia. It is a fuming, yellowish liquid; sp. gr. 2.28; boils at 120° (248°F.).

Analytical Characters.—**STANNOUS.**—(1) Potash or soda: white ppt.; soluble in excess; the solution deposits Sn when boiled. (2) Ammonium hydroxid: white ppt; insoluble in excess; turns olive-brown when the liquid is boiled. (3) Hydrogen sulfid: dark brown ppt.; soluble in KHO , alkaline sulfids, and hot H_2O . (4) Mercuric chlorid: white ppt., turning gray and black. (5) Auric chlorid: purple or brown ppt., in presence of small quantities of HNO_3 . (6) Zinc: deposit of Sn .

STANNIC.—(1) Potash or ammonia: white ppt.; soluble in excess. (2) Hydrogen sulfid: yellow ppt.; soluble in alkalies, alkaline sulfids, and hot HCl . (3) Sodium hyposulfite: yellow ppt., when heated.

VII. PLATINUM GROUP.

PALLADIUM. PLATINUM.

VIII. RHODIUM GROUP.

RHODIUM. RUTHENIUM. IRIIDIUM

The elements of these two groups, together with osmium, are usually classed as "metals of the platinum ores." They all form hydrates (or salts representing them) having acid properties. Osmium has been removed, because the relations existing between its compounds, and those of molybdenum and tungsten, are much closer than those which they exhibit to the compounds of these groups. The separation of the remaining platinum metals into two groups is based upon resemblances in the composition of their compounds, as shown in the following table.

CHLORIDS.

PdCl_2 PtCl_2	RhCl_2 RuCl_2 ?
PdCl_4 PtCl_4	— RuCl_4 IrCl_4
— —	Rh_2Cl_6 Ru_2Cl_6 Ir_2Cl_6

OXIDS.

PdO PtO	RhO RuO IrO
— —	Rh ₂ O ₃ Ru ₂ O ₃ Ir ₂ O ₃
PdO ₂ PtO ₂	RhO ₂ RuO ₂ IrO ₂
— —	RhO ₃ RuO ₃ IrO ₃
— —	— RuO ₄ —

PLATINUM.

Symbol=Pt—*Atomic weight*=194.8 (O=16:194.8 ; H=1:193.25)
—*Molecular weight*=390 (†)—*Sp. gr.*=21.1–21.5.

Occurrence.—Free and alloyed with Os, Ir, Pd, Rh, Ru, Fe, Pb, Au, Ag, and Cu.

Properties.—The compact metal has a silvery luster; softens at a white heat; may be welded; fuses with difficulty; highly malleable, ductile and tenacious. **Spongy platinum** is a grayish, porous mass, formed by heating the double chlorid of Pt and NH₄. **Platinum black** is a black powder, formed by dissolving PtCl₂ in solution of potash, and heating with alcohol. Both platinum black and platinum sponge are capable of condensing large quantities of gas, and act as indirect oxidants.

Platinum is not oxidized by air or O; it combines directly with Cl, P, As, Si, S, and C; is not attacked by acids, except aqua regia, in which it dissolves. It forms fusible alloys when heated with metals or reducible metallic oxids. It is attacked by mixtures liberating Cl, and by contact with heated phosphates, silicates, hydroxids, nitrates, or carbonates of the alkaline metals.

Platinic Chlorid—*Tetrachlorid* or *perchlorid* of *platinum*—PtCl₄—336.6—When Pt is dissolved in aqua regia and the solution is evaporated, red, deliquescent crystals of **hydrochloroplatinic acid**, H₂PtCl₆, are obtained. These, when heated in chlorin, yield yellow, non-deliquescent crystals of platinic chlorid, PtCl₄. Hydrochloroplatinic acid is a strong dibasic acid, the platinum being in the anion, which forms crystalline **chloroplatinates** with the alkaline metals, NH₄, and a great number of nitrogenous organic bases. The formation of the K and NH₄ salts is utilized to test for those cations, and the formation of the organic compounds is resorted to for the identification and analysis of these bases.

CLASS V.—BASYLOUS ELEMENTS.

Elements whose Oxide unite with Water to form Bases; never to form Acids.
Which form Oxysalts.

The elements of this class are essentially basic and electropositive. In solutions of their compounds they never occur in an anion, simple or compound, but always constitute simple cations.

I. SODIUM GROUP.

Alkali Metals.

LITHIUM—SODIUM—POTASSIUM—RUBIDIUM—CÆSIUM—SILVER.

Each of the elements of this group forms a single chlorid, $M'Cl$, and one or more oxids, the most stable of which has the composition M'_2O . They are, therefore, univalent. Their hydroxids, $M'HO$, are more or less alkaline and have markedly basic characters. Silver resembles the other members of the group in chemical properties, although it does not in physical characters.

The name "alkali," first applied to "potash" from wood ashes (p. 225) is now used to designate substances which are strongly basic, are alkaline in reaction, and saponify fats. The **caustic alkalis** are the hydroxids of K and Na, the **carbonated alkalis** are their carbonates. **Volatile alkali** is ammonium hydroxid or carbonate.

LITHIUM.

Symbol=Li—*Atomic weight*=7 (O=16:7.03; H=1:6.97)—*Molecular weight*=14 (1)—*Sp. gr.*=0.589—*Fuses at* 180° (356° F.)—*Discovered by* Arfvedson in 1817—*Name from* λίθος=stony.

Occurrence.—Widely distributed in small quantity; in many minerals and mineral waters; in the ash of tobacco and other plants; in the milk and blood.

Properties.—A silver-white, ductile, volatile metal; the lightest of the solid elements; burns in air with a crimson flame; decomposes H_2O at ordinary temperatures, without igniting.

Lithium Chlorid.— $LiCl$ —43.5—crystallizes in deliquescent, regular octahedra; very soluble in H_2O and in alcohol.

Lithium Bromid—*Lithii bromidum*—(U. S.)— $LiBr$ —87—is formed by decomposing lithium sulfate with potassium bromid; or by saturating a solution of HBr with lithium carbonate. It crystallizes in very deliquescent, soluble needles.

Lithium Carbonate—*Lithii carbonas* (U. S.; Br)— Li_2CO_3 —74—

is a white, sparingly soluble, alkaline, amorphous powder. With uric acid it forms lithium urate (q. v.).

Analytical Characters.—(1) Ammonium carbonate: white ppt. in concentrated solutions; not in dilute solutions, or in presence of ammoniacal salts. (2) Sodium phosphate: white ppt. in neutral or alkaline solution; soluble in acids and in solutions of ammoniacal salts. (3) It colors the Bunsen flame red; and exhibits a spectrum of two lines— $\lambda=6705$ and 6102 (Fig. 14, No. 4, p. 35).

SODIUM.

Symbol = Na (*Natrium*)—*Atomic weight* = 23 ($O = 16:23.05$; $H = 1:22.87$)—*Molecular weight* = 46 (?)—*Sp. gr.* = 0.972—*Fuses at* 95.6° (204.1° F.)—*Boils at* 742° (1368° F.)—*Discovered by* Davy, 1807.

Occurrence.—As chlorid, very abundantly and widely distributed; also as carbonate, nitrate, sulfate, borate, etc.

Preparation.—By heating a mixture of dry sodium carbonate, chalk, and charcoal to whiteness in iron retorts. It is now manufactured by the electrolysis of fused NaHO.

Properties.—A silver-white metal, rapidly tarnished, and coated with a yellow film in air. Waxy at ordinary temperatures; volatile at a white heat, forming a colorless vapor, which burns in air with a yellow flame.

It oxidizes in air, and is usually preserved under naphtha. It burns with a yellow flame. It combines directly with Cl, Br, I, S, P, As, Pb and Sn. It decomposes water with evolution of hydrogen: $Na_2 + 2H_2O = 2NaHO + H_2$. Because of this and other similar reactions, metallic sodium, either as such or in the diluted form of sodium amalgam, is largely used to effect reductions.

Oxids.—Two oxids are known: **Sodium monoxid**— Na_2O —a grayish white mass; formed when Na is burnt in dry air, or by the action of Na on NaHO. **Sodium dioxid**— Na_2O_2 —a white solid, formed when Na is heated in dry air to 200° (392° F.). Sodium dioxid, or peroxid, is now manufactured by oxidizing the fused metal in dry air or oxygen, and is used as a bleaching and oxidizing agent. It is a yellowish white, amorphous, very hygroscopic powder. If the temperature be kept low it dissolves in dilute acids, forming a strong solution of hydrogen peroxid: $Na_2O_2 + 2HCl = 2NaCl + H_2O_2$. With water it produces a great elevation of temperature and liberates nascent oxygen: $2Na_2O_2 + 2H_2O = 4NaHO + O_2$. With magnesium sulfate it forms magnesium peroxid, a non-alkaline oxydant: $Na_2O_2 + MgSO_4 = Na_2SO_4 + MgO_2$.

Sodium Hydroxid—*Sodium hydrate*—**Caustic Soda**—**Soda** (U.S.)—**Soda caustica** (Br.)— NaHO —40—is formed: (1) When H_2O is decomposed by Na ; (2) by decomposing sodic carbonate by calcium hydroxid: $\text{Na}_2\text{CO}_3 + \text{CaH}_2\text{O}_2 = \text{CO}_2\text{Ca} + 2\text{NaHO}$ (soda by lime); (3) in the same manner as in (2), using barium hydroxid in place of lime (soda by baryta). It frequently contains considerable quantities of *As.* (4) Caustic soda is now largely manufactured by electrolytic decomposition of NaCl . The Castner process is the one usually adopted. In it, by a rocking arrangement, mercury, as the cathode, first takes up the liberated sodium, and is then brought in contact with a suitable quantity of water. The reactions are: $2\text{NaCl} = \text{Na}_2 + \text{Cl}_2$, and $\text{Na}_2 + 2\text{H}_2\text{O} = 2\text{NaHO} + \text{H}_2$. (See Chlorin.)

It is an opaque, white, fibrous, brittle solid; fusible below redness; sp. gr. 2.00; very soluble in H_2O , forming strongly alkaline and caustic solutions (*soda lye* and *liq. sodæ*). When exposed to air, solid or in solution, it absorbs H_2O and CO_2 , and is converted into carbonate. Its solutions attack glass.

Sodium Chlorid—**Common salt**—**Sea salt**—**Table salt**—**Sodii chloridum** (U. S.; Br.)— NaCl —58.5—occurs very abundantly in nature, deposited in the solid form as **rock salt**; in solution in all natural waters, especially in sea and mineral spring waters; in suspension in the atmosphere; and as a constituent of almost all animal and vegetable tissues and fluids. It is formed in an infinite variety of chemical reactions. It is obtained from rock salt, or from the waters of the sea, or of saline springs; and is the source from which all the Na compounds are usually obtained, directly or indirectly.

It crystallizes in anhydrous, white cubes, or octahedra; sp. gr. 2.078; fuses at a red heat, and crystallizes on cooling; sensibly volatile at a white heat; quite soluble in H_2O , the solubility varying but slightly with the variations of temperature. Dilute solutions yield almost pure ice on freezing. It is precipitated from concentrated solutions by HCl . It is insoluble in absolute alcohol; sparingly soluble in dilute spirit. It is decomposed by H_2SO_4 with formation of HCl and sodium sulfate: $2\text{NaCl} + \text{H}_2\text{SO}_4 = 2\text{HCl} + \text{Na}_2\text{SO}_4$.

Sodium Bromid—**Sodii bromidum** (U. S.)— NaBr —103—is formed by dissolving Br in solution of NaHO to saturation; evaporating; calcining at dull redness; redissolving, filtering, and crystallizing. It crystallizes in anhydrous cubes; quite soluble in H_2O , soluble in alcohol.

Sodium Iodid—**Sodii iodidum** (U. S.)— NaI —150—is prepared by heating together H_2O , Fe , and I in fine powder; filtering; adding an equivalent quantity of sodium sulfate, and some slacked lime, boiling, decanting and evaporating. Crystallizes in anhydrous cubes; very soluble in H_2O ; soluble in alcohol.

Sodium Nitrate—Cubic or Chili saltpeter—*Sodii nitras* (U. S.); *Sodæ nitras* (Br.)— NaNO_3 —85—occurs in natural deposits in Chili and Peru. It crystallizes in anhydrous, deliquescent rhombohedra; cooling and somewhat bitter in taste; fuses at 310° (590° F.); very soluble in H_2O . Heated with H_2SO_4 , it is decomposed, yielding HNO_3 and hydrosodic sulfate: $\text{H}_2\text{SO}_4 + \text{NaNO}_3 = \text{HNaSO}_4 + \text{HNO}_3$. This reaction is that used for obtaining HNO_3 .

Sulfates.—**Monosodic Sulfate**—*Hydrosodic sulfate*—*Acid sodium sulfate*—*Bisulfate*— HNaSO_4 —120—crystallizes in long, four-sided prisms; is unstable and decomposed by air, H_2O or alcohol, into H_2SO_4 and Na_2SO_4 . Heated to dull redness it is converted into **sodium pyrosulfate**, $\text{Na}_2\text{S}_2\text{O}_7$, corresponding to Nordhausen sulfuric acid.

Disodic Sulfate—*Sodic sulfate*—*Neutral sodium sulfate*—**Glauber's salt**—*Sodii sulfas* (U. S.); *sodæ sulfas* (Br.)— $\text{Na}_2\text{SO}_4 + n\text{Aq}$ —142 + n 18—occurs in nature in solid deposits, and in solution in natural waters. It is obtained as a secondary product in the manufacture of HCl , by the action of H_2SO_4 on NaCl , the decomposition occurring according to the equation: $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$, if the temperature be raised sufficiently. At lower temperatures, the monosodic salt is produced, with only half the yield of HCl : $\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$.

It crystallizes with 7 Aq, from saturated or supersaturated solutions at 5° (41° F.); or, more usually, with 10 Aq. As usually met with it is in large, colorless, oblique, rhombic prisms with 10 Aq; which effloresce in air, and gradually lose all their Aq. It fuses at 33° (91.4° F.) in its Aq, which it gradually loses. If fused at 33° (91.4° F.), and allowed to cool, it remains liquid in *supersaturated* solution, from which it is deposited, the entire mass becoming solid, on contact with a small particle of solid matter. It dissolves in HCl with considerable diminution of temperature.

Sodium Sulfite—*Sodii sulfis* (U. S.)— $\text{Na}_2\text{SO}_3 + 7\text{Aq}$ —126 + 126—is formed by passing SO_2 over crystallized Na_2CO_3 . It crystallizes in efflorescent, oblique prisms; quite soluble in H_2O , forming an alkaline solution. It acts as a reducing agent.

Sodium Thiosulfate—*Sodium hyposulfite*—*Sodii hyposulfis* (U. S.)— $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{Aq}$ —158 + 90—is obtained by dissolving S in hot concentrated solution of Na_2SO_3 , and crystallizing.

It forms large, colorless, efflorescent prisms; fuses at 45° (113° F.); very soluble in H_2O , insoluble in alcohol. Its solutions precipitate alumina from solutions of Al salts, without precipitating Fe or Mn; they dissolve many compounds insoluble in H_2O ; cuprous hydroxid, iodids of Pb, Ag and Hg, sulfids of Ca and Pb. It acts as a disinfectant and antiseptic. H_2SO_4 decomposes $\text{Na}_2\text{S}_2\text{O}_3$ according

to the equation: $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{SO}_2 + \text{S} + \text{H}_2\text{O}$; and most other acids behave similarly. Oxalic, and a few other acids, decompose the thiosulfate with formation of H_2S as well as SO_2 and S .

Silicates.—Quite a number of silicates of Na are known. If silica and Na_2CO_3 be fused together, the residue extracted with H_2O , and the solution evaporated, a transparent, glass-like mass, soluble in warm water, remains; this is **soluble glass** or **water glass**. Exposed to air in contact with stone, it becomes insoluble, and forms an impermeable coating.

Phosphates.—**Trisodic Phosphate**—*Basic sodium phosphate*— $\text{Na}_3\text{PO}_4 + 12 \text{ Aq} - 164 + 216$ —is obtained by adding NaHO to disodic phosphate solution, and crystallizing. It forms six-sided prisms; quite soluble in H_2O . Its solution is alkaline, and, on exposure to air, absorbs CO_2 , with formation of HNa_2PO_4 and Na_2CO_3 .

Disodic Phosphate—*Hydro-disodic phosphate*—*Neutral sodium phosphate*—*Phosphate of soda*—**Sodii phosphas** (U. S.); **sodæ phosphas** (Br.)— $\text{HNa}_2\text{PO}_4 + 12 \text{ Aq} - 142 + 216$ —is obtained by converting tricalcic phosphate into monocalcic phosphate, and decomposing that salt with sodium carbonate: $\text{Ca}(\text{PO}_4\text{H}_2)_2 + 2\text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 + 2\text{HNa}_2\text{PO}_4$.

Below 30° (86° F.) it crystallizes in oblique rhombic prisms, with 12 Aq; at 33° (91.4° F.) it crystallizes with 7 Aq. The salt with 12 Aq effloresces in air, and parts with 5 Aq; and is very soluble in H_2O . The salt with 7 Aq is not efflorescent, and less soluble in H_2O . Its solutions are faintly alkaline.

Monosodic Phosphate—*Acid sodium phosphate*— $\text{H}_2\text{NaPO}_4 + \text{Aq} - 120 + 18$ —crystallizes in rhombic prisms; forming acid solutions. At 100° (212° F.) it loses Aq; at 200° (392° F.) it is converted into **acid pyrophosphate**, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$; and at 204° (399.2° F.) into the **metaphosphate**, NaPO_3 .

Sodium Arsenites.—The disodic arsenite, Na_2HAsO_3 , is obtained as a viscous mass by fusing together 1 molecule of As_2O_3 and 2 molecules of Na_2CO_3 without contact of air. The monosodic arsenite, NaH_2AsO_3 , is formed when an aqueous solution of Na_2CO_3 is boiled with As_2O_3 . By prolonged boiling this is converted into the pyroarsenite, $\text{Na}_2\text{H}_2\text{As}_2\text{O}_5$, and this into the metarsenite, NaAsO_2 , by progressive loss of water. Sodium arsenites exist in embalming liquids and are used in dyeing.

Sodium Arsenates.—The three arsenates, NaH_2AsO_4 , Na_2HAsO_4 and Na_3AsO_4 corresponding to the phosphates, are known, and are used in dyeing processes.

Disodic Tetraborate—*Sodium pyroborate*—*Borate of sodium*—**Borax**—*Tincal*—**Sodii boras** (U. S.); **Borax** (Br.)— $\text{Na}_2\text{B}_4\text{O}_7 + 10 \text{ Aq} - 202 + 180$ —is prepared by boiling boric acid with Na_2CO_3 and crys-

tallizing. It crystallizes in hexagonal prisms with 10 Aq; permanent in moist air, but efflorescent in dry air; or in regular octahedra with 5 Aq, permanent in dry air. Either form, when heated, fuses in its Aq, swells considerably; at a red heat becomes anhydrous; and, on cooling, leaves a transparent, glass-like mass. When fused it is capable of dissolving many metallic oxids, forming variously colored masses, hence its use as a flux and in blow-pipe analysis.

Sodium Hypochlorite— NaClO —74.5—only known in solution—**Liq. sodæ chloratæ** (U. S.; Br.) or **Labarraque's solution**—obtained by decomposing a solution of chlorid of lime by Na_2CO_3 . It is a valuable source of Cl, and is used as a bleaching and disinfecting agent.

Sodium Chlorate—**Sodii chloras** (U. S.)— NaClO_3 —106.5—is manufactured industrially by treating milk of lime with Cl. The solution of calcium chlorid and chlorate so obtained is treated with Na_2SO_4 , after removal of part of the CaCl_2 by concentration and cooling to 12° (53.6° F.). The NaClO_3 and NaCl formed are separated by taking advantage of the greater solubility of the former. NaClO_3 is soluble in its own weight of H_2O at 20° (68° F.).

Sodium Manganate— $\text{Na}_2\text{MnO}_4 + 10 \text{ Aq}$ — $164 + 180$ —faintly colored crystals, forming a green solution with H_2O —**Condy's green disinfectant**.

Sodium Permanganate— $\text{Na}_2\text{Mn}_2\text{O}_8$ —282—prepared in the same way as the K salt (*q. v.*), which it resembles in its properties. It enters into the composition of **Condy's fluid**, and of "chlorozone," which contains $\text{Na}_2\text{Mn}_2\text{O}_8$ and NaClO .

Sodium Acetate—**Sodii acetat** (U. S.); **Sodæ acetat** (Br.)— $\text{NaC}_2\text{H}_3\text{O}_2 + 3 \text{ Aq}$ — $82 + 54$ —crystallizes in large, colorless prisms; acid and bitter in taste; quite soluble in H_2O , soluble in alcohol; loses its Aq in dry air, and absorbs it again from moist air. Heated with soda lime, it yields marsh gas. The anhydrous salt, heated with H_2SO_4 , yields glacial acetic acid.

Carbonates.—Three are known: Na_2CO_3 , HNaCO_3 , and $\text{H}_2\text{Na}_4(\text{CO}_3)_3$.

Disodic Carbonate—*Neutral Carbonate*—**Soda**—**Sal soda**—**Washing Soda**—**Soda crystals**—**Sodii carbonas** (U. S.); **Sodæ carbonas** (Br.)— $\text{Na}_2\text{CO}_3 + 10 \text{ Aq}$ — $106 + 180$ —industrially the most important of the Na compounds, is manufactured by Leblanc's or Solvay's processes; or from *cryolite*, a native fluorid of Na and Al.

Leblanc's process, in its present form, consists of three distinct processes: (1) The conversion of NaCl into the sulfate, by decomposition by H_2SO_4 . (2) The conversion of the sulfate into carbonate, by heating a mixture of the sulfate with calcium carbonate and charcoal. The product of this reaction, known as **black ball soda**, is a

mixture of sodium carbonate with charcoal and calcium sulfid and oxid. (3) The purification of the product obtained in (2). The ball black is broken up, disintegrated by steam, and lixiviated. The solution on evaporation yields the **soda salt** or **soda** of commerce.

Of late years Leblanc's process has been in great part replaced by Solvay's method, or the *ammonia process*, which is more economical, and yields a purer product. In this process sodium chlorid and ammonium bicarbonate react upon each other, with production of the sparingly soluble sodium bicarbonate, and the very soluble ammonium chlorid. The sodium bicarbonate is then simply collected, dried, and heated, when it is decomposed into Na_2CO_3 , H_2O , and CO_2 . Sodium carbonate is also made from cryolite, a double fluorid of sodium and aluminium found in Greenland. This is heated with limestone when: $\text{Al}_2\text{Na}_6\text{F}_{12} + 6\text{CaCO}_3 = 6\text{CaF}_2 + 6\text{CO}_2 + \text{Na}_6\text{Al}_2\text{O}_6$. The sodium aluminate is extracted with water and the solution treated with carbon dioxide (obtained in the first reaction) when: $\text{Na}_6\text{Al}_2\text{O}_6 + 3\text{H}_2\text{O} + 3\text{CO}_2 = 3\text{Na}_2\text{CO}_3 + \text{Al}_2(\text{OH})_6$.

The anhydrous carbonate, *Sodii carbonas exsiccatus* (U. S.), Na_2CO_3 , is formed, as a white powder, by calcining the crystals. It fuses at dull redness, and gives off a little CO_2 . It combines with and dissolves in H_2O with elevation of temperature.

The crystalline sodium carbonate, $\text{Na}_2\text{CO}_3 + 10\text{Aq}$, forms large rhombic crystals, which effloresce rapidly in dry air; fuse in their Aq at 34° (93.2° F.); are soluble in H_2O , most abundantly at 38° (100.4° F.). The solutions are alkaline in reaction.

Monosodic Carbonate—*Hydrosodic carbonate*—**Bicarbonate of soda**—*Acid carbonate of soda*—*Vichy salt*—**Sodii bicarbonas** (U. S.)—**Sodæ bicarbonas** (Br.)— NaHCO_3 —84—exists in solution in many mineral waters. It is obtained by the action of CO_2 upon the disodic salt in the presence of H_2O ; or, as above described, by the Solvay method.

It crystallizes in rectangular prisms, anhydrous and permanent in dry air. In damp air it gives off CO_2 , and is converted into the **sesquicarbonate**, $\text{Na}_4\text{H}_2(\text{CO}_3)_3$. When heated it gives off CO_2 and H_2O , and leaves the disodic carbonate. Quite soluble in water; above 70° (158° F.) the solution gives off CO_2 . The solutions are alkaline.

Analytical Characters.—(1) Hydrofluosilicic acid: gelatinous ppt., if not too dilute. (2) Potassium pyroantimonate, in neutral solution, and in absence of metals other than K and Li: a white, flocculent ppt.; becoming crystalline on standing. (3) Periodic acid in excess: white ppt., in not too dilute solutions. (4) Colors the Bunsen flame yellow, and shows a brilliant double line at $\lambda=5895$ and 5889 (Fig. 14, No. 2, p. 35).

POTASSIUM.

Symbol = K (*Kalium*)—*Atomic weight* = 39 (O = 16.39.15 ; H = 1.38.84)—*Molecular weight* = 78 (?)—*Sp. gr.* = 0.865—*Fuses at* 62.5° (144.5° F.)—*Boils at* 667° (1233° F.)—*Discovered by* Davy, 1807—*Names from* pot ash, and Kali=ashes (Arabic).

Potassium silicates are widely distributed in rocks and minerals. The ash of plants contain about 10 per cent. of potassium carbonate, and this was formerly the chief source of the K compounds. Almost all of these are now derived from the deposits of *carnallite*: KCl , $\text{MgCl}_2 + 6\text{Aq.}$ and allied minerals at Stassfurt in Germany.

It is prepared by a process similar to that followed in obtaining Na; is a silver-white metal; brittle at 0° (32° F.); waxy at 15° (59° F.); fuses at 62.5° (144.5° F.); distils in green vapors at a red heat, condensing in cubic crystals. It is also obtained by electrolysis of fused KHO.

It is the only metal which oxidizes at low temperatures in dry air, in which it is rapidly coated with a white layer of oxid or hydroxid, and frequently ignites, burning with a violet flame. It must, therefore, be kept under naphtha. It decomposes H_2O , or ice, with great energy, the heat of the reaction igniting the liberated H. It combines with Cl with incandescence, and also unites directly with S, P, As, Sb, and Sn. Heated in CO_2 it is oxidized, and liberates C.

Oxids.—Three are known: K_2O ; K_2O_2 ; and K_2O_4 .

Potassium Hydroxid—*Potassium hydrate*—*Potash*—*Potassa*—*Common caustic*—*Potassa* (U. S.)—*Potassa caustica* (Br.)—KHO—56—is obtained by processes similar to those used in manufacturing NaHO. It is purified by solution in alcohol, evaporation and fusion in a silver basin, and casting in silver moulds—*potash by alcohol*; it is then free from KCl and K_2SO_4 , but contains small quantities of K_2CO_3 , and frequently As.

It is usually met with in cylindrical sticks, hard, white, opaque, and brittle. The KHO by alcohol has a bluish tinge, and a smoother surface than the common; sp. gr. 2.1; fuses at dull redness; is freely soluble in H_2O , forming a strongly alkaline and caustic liquid; less soluble in alcohol. In air, solid or in solution, it absorbs H_2O and CO_2 , and is converted into K_2CO_3 . Its solutions dissolve Cl, Br, I, S, and P. It decomposes the ammoniacal salts, with liberation of NH_3 ; and the salts of many of the metals, with formation of a K salt, and a metallic hydroxid. It dissolves the proteins, and, when heated, decomposes them with formation of leucin, tyrosin, etc. It oxidizes the carbohydrates with formation of potassium oxalate and carbonate. It decomposes the fats with formation of soft soaps.

Sulfids.—Five are known: K_2S , K_2S_2 , K_2S_3 , K_2S_4 , and K_2S_5 ; also a sulfhydrate: KHS .

Potassium Monosulfid— K_2S —110—is formed by the action of KHO on KHS . **Potassium Disulfid**— K_2S_2 —142—is an orange-colored solid, formed by exposing an alcoholic solution of KHS to the air. **Potassium Trisulfid**— K_2S_3 —174—a brownish yellow mass, obtained by fusing together K_2CO_3 and S in the proportion: $4K_2CO_3 + 10S = SO_4K_2 + 3K_2S_3 + 4CO_2$. **Potassium Pentasulfid**— K_2S_5 —238—is formed, as a brown mass, when K_2CO_3 and S are fused together in the proportion: $4K_2CO_3 + 16S = 4CO_2 + 3K_2S_5 + K_2SO_4$. **Liver of Sulfur**—*hepar sulfuris*—*potassii sulfuratum* (U. S.; Br.)—is a mixture of K_2S_3 and K_2S_5 .

Potassium Sulfhydrate— KHS —72—is formed by saturating a solution of KHO with H_2S .

Potassium Chlorid—*Sal digestivum Sylvii*— KCl —74.5—exists in nature, either pure or mixed with other chlorids; principally as *carallite*, KCl , $MgCl_2 + 6Aq$. It crystallizes in anhydrous, permanent cubes, soluble in H_2O .

Potassium Bromid—*Potassii bromidum* (U. S.; Br.)— KBr —119—is formed either by decomposing $FeBr_2$ by K_2CO_3 , or by dissolving Br in solution of KHO . In the latter case the *bromate* formed is converted into KBr , by calcination. It crystallizes in anhydrous cubes or tables; has a sharp, salty taste; very soluble in H_2O , sparingly so in alcohol. It is decomposed by Cl with liberation of Br .

Potassium Iodid—*Potassii iodidum* (U. S.; Br.)— KI —166—is obtained by saturating KHO solution with I , evaporating, and calcining the resulting mixture of iodid and iodate with charcoal. It frequently contains iodate and carbonate. It crystallizes in cubes, transparent if pure; permanent in air; anhydrous; soluble in H_2O and in alcohol. It is decomposed by Cl , HNO_3 and HNO_2 , with liberation of I . It combines with other iodids to form double iodids. Its solutions dissolve iodine and many metallic iodids.

Potassium Nitrate—*Nitre*—*Saltpeter*—*Potassii nitras* (U. S.); *Potassæ nitras* (Br.)— KNO_3 —101—occurs in nature, and is produced artificially, as a result of the decomposition of nitrogenized organic substances. It is usually obtained by decomposing native $NaNO_3$ by boiling solution of K_2CO_3 or KCl .

It crystallizes in six-sided, rhombic prisms, grooved upon the surface; soluble in H_2O , with depression of temperature; more soluble in H_2O containing $NaCl$; very sparingly soluble in alcohol; fuses at 350° ($662^\circ F.$) without decomposition; gives off O , and is converted into nitrite below redness; more strongly heated, it is decomposed into N , O , and a mixture of K oxids. It is a valuable oxidant at high temperatures. Heated with charcoal it deflagrates.

Gunpowder is an intimate mixture of KNO_3 with S and C, in such proportion that the KNO_3 yields all the O required for the combustion of the S and C.

Potassium Hypochlorite— KClO —90.5—is formed in solution by imperfect saturation of a cooled solution of KHO with hypochlorous acid. An impure solution is used in bleaching: **Javelle water**.

Potassium Chlorate—**Potassii chloras** (U. S.)—**Potassæ chloras** (Br.)— KClO_3 —122.5—is prepared: (1) by passing Cl through a solution of KHO; (2) by passing Cl over a mixture of milk of lime and KCl, heated to 60° (140° F.); (3) by electrolysis of KCl. By electrolytic action the KCl is split into its ions: $2\text{KCl}=2\text{K}+2\text{Cl}$; these, by secondary reactions with H_2O , produce KClO : $\text{K}_2+2\text{H}_2\text{O}=2\text{KHO}+\text{H}_2$, and $2\text{KHO}+\text{Cl}_2=2\text{KClO}+\text{H}_2$, and at the temperature generated, the KClO yields KClO_3 : $2\text{KClO}+\text{H}_2\text{O}=\text{KClO}_3+\text{KCl}+\text{H}_2$. It crystallizes in transparent, anhydrous plates, soluble in H_2O ; sparingly soluble in weak alcohol.

It fuses at 400° (752° F.). If further heated, it is decomposed into KCl and perchlorate, and at a still higher temperature the perchlorate is decomposed into KCl and O: $2\text{KClO}_3=\text{KClO}_4+\text{KCl}+\text{O}_2$, and $\text{KClO}_4=\text{KCl}+2\text{O}_2$. It is a valuable source of O, and a more active oxidant than KNO_3 . When mixed with readily oxidizable substances, C, S, P, sugar, tannin, resins, etc., the mixtures explode when subjected to shock. With strong H_2SO_4 it gives off Cl_2O_4 , an explosive yellow gas. It is decomposed by HNO_3 with formation of KNO_3 , KClO_4 , and liberation of Cl and O. Heated with HCl it gives off a mixture of Cl and Cl_2O_4 , the latter acting as an energetic oxidant in solutions in which it is generated.

Sulfates.—**Dipotassic sulfate**—*Potassium sulfate*—**Potassii sulfas** (U. S.)—**Potassæ sulfas** (Br.)— K_2SO_4 —174—occurs native; in the ash of many plants; and in solution in mineral waters. It crystallizes in right rhombic prisms; hard; permanent in air; salt and bitter in taste; soluble in H_2O .

Monopotassic Sulfate.—*Hydropotassic sulfate*—*Acid sulfate*— KHSO_4 —136—is formed as a by-product in the manufacture of HNO_3 . When heated it loses H_2O , and is converted into the **pyrosulfate**, $\text{K}_2\text{S}_2\text{O}_7$, which, at a higher temperature, is decomposed into K_2SO_4 and SO_3 .

Dipotassic Sulfite—*Potassic sulfite*—**Potassii sulfis** (U. S.)— K_2SO_3 —158—is formed by saturating solution of K_2CO_3 with SO_2 , and evaporating over H_2SO_4 . It crystallizes in oblique rhombohedra; soluble in H_2O . Its solution absorbs O from the air, with formation of K_2SO_4 .

Potassium Dichromate—*Bichromate of potash*—**Potassii bichromas** (U. S.)—**Potassæ bichromas** (Br.)— $\text{K}_2\text{Cr}_2\text{O}_7$ —294.8—is

formed by heating a mixture of *chrome iron ore* with KNO_3 , or K_2CO_3 in air; extracting with H_2O ; neutralizing with dilute H_2SO_4 ; and evaporating. It forms large, reddish-orange colored prismatic crystals; soluble in H_2O ; fuses below redness, and at a higher temperature is decomposed into O, potassium chromate, and chromic oxid. Heated with HCl , it gives off Cl.

Potassium Permanganate—**Potassii permanganas** (U. S.); **Potassæ permanganas** (Br.)— $\text{K}_2\text{Mn}_2\text{O}_8$ —314—is obtained by fusing a mixture of manganese dioxid, KHO , and KClO_3 , and evaporating the solution to crystallization; K_2MnO_4 , and KCl are first formed; on boiling with H_2O , the manganate is decomposed into $\text{K}_2\text{Mn}_2\text{O}_8$, KHO and MnO_2 .

It crystallizes in dark prisms, almost black, with greenish reflections, which yield a red powder when broken. Soluble in H_2O , communicating to it a red color, even in very dilute solution. It is a most valuable oxidizing agent. With organic matter its solution is turned to green, by the formation of the manganate, or deposits the brown sesquioxid of manganese, according to the nature of the organic substance. In some instances the reaction takes place best in the cold, in others under the influence of heat; in some better in acid solutions, in others in alkaline solutions. Mineral reducing agents act more rapidly. Its oxidizing powers render its solutions valuable as disinfectants.

Potassium Acetate—**Potassii acetas** (U. S.); **Potassæ acetas** (Br.)— $\text{KC}_2\text{H}_3\text{O}_2$ —110—exists in the sap of plants; and it is by its calcination that the major part of the carbonate of wood ashes is formed. It is prepared by neutralizing acetic acid with K_2CO_3 or KHCO_3 .

It forms crystalline needles, deliquescent, and very soluble in H_2O ; less soluble in alcohol. Its solutions are faintly alkaline.

Carbonates.—**Dipotassic Carbonate**—**Potassic Carbonate**—**Salt of tartar**—**Pearl ash**—**Potassii carbonas** (U. S.); **Potassæ carbonas** (Br.)— K_2CO_3 —138—exists in mineral waters, and in the animal economy. It is prepared industrially, in an impure form, known as **potash** or **pearlash**, from wood ashes, from the molasses of beet sugar, and from the native Stassfurth chlorid. It is obtained pure by decomposing the monopotassic salt, purified by several recrystallizations, by heat; or by calcining a potassium salt of an organic acid. Thus cream of tartar, mixed with nitre and heated to redness, yields a black mixture of C and K_2CO_3 , called **black flux**; on extracting which with H_2O , a pure carbonate, known as **salt of tartar**, is dissolved.

Anhydrous, it is a white, granular, deliquescent, very soluble powder. At low temperatures it crystallizes with 2Aq . Its solution is alkaline.

Monopotassic Carbonate—*Hydropotassic carbonate*—**Bicarbonate**—**Potassii bicarbonas** (U. S.); **Potassæ bicarbonas** (Br.)— HKCO_3 —100—is obtained by dissolving K_2CO_3 in H_2O , and saturating the solution with CO_2 . It crystallizes in oblique rhombic prisms, much less soluble than the carbonate. In solution, it is gradually converted into the dipotassic salt when heated, when brought into a vacuum, or when treated with an inert gas. The solutions are alkaline in reaction and in taste, but are not caustic.

The substance used in baking, under the name **salæratus**, is this or the corresponding Na salt, usually the latter. Its extensive use in some parts of the country is undoubtedly in great measure the cause of the prevalence of dyspepsia. When used alone in baking, it "raises" the bread by decomposition into carbon dioxid and dipotassic (or disodic) carbonate, the latter producing disturbances of digestion by its strong alkaline reaction.

Monopotassic Oxalate—*Hydropotassic oxalate*—*Binoxalate of potash*— KHC_2O_4 —128—forms transparent, soluble, acid needles. It occurs along with the **quadroxalate** HKC_2O_4 , $\text{H}_2\text{C}_2\text{O}_4 + 2\text{Aq}$, in **salt of lemon** or **salt of sorrel**, used in straw bleaching, and for the removal of ink-stains, etc. It closely resembles Epsom salt in appearance, and has been fatally mistaken for it.

Tartrates.—**Dipotassic Tartrate**—*Potassic tartrate*—**Soluble tartar**—*Neutral tartrate of potash*—**Potassii tartras** (U. S.)—**Potassæ tartras** (Br.)— $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ —226—is prepared by neutralizing the hydropotassic salt with potassium carbonate. It forms a white, crystalline powder, very soluble in H_2O , the solution being dextrogyrous, $[\alpha]_D = +28.48^\circ$; soluble in alcohol. Acids, even acetic, decompose its solution, with precipitation of the monopotassic salt.

Monopotassic Tartrate—*Hydropotassic tartrate*—**Cream of tartar**—**Potassii bitartras** (U. S.)—**Potassæ bitartras** (Br.)— $\text{HKC}_4\text{H}_4\text{O}_6$ —188.—During the fermentation of grape juice, as the proportion of alcohol increases, crystalline crusts collect in the cask. These constitute the **crude tartar**, or **argol**, of commerce, which is composed, in great part, of monopotassic tartrate, with some calcium tartrate and coloring matter. The crude product is purified by repeated crystallization from boiling H_2O , decolorizing with animal charcoal, digesting the purified tartar with HCl at 20° (68°F.), washing with cold H_2O , and crystallizing from hot H_2O .

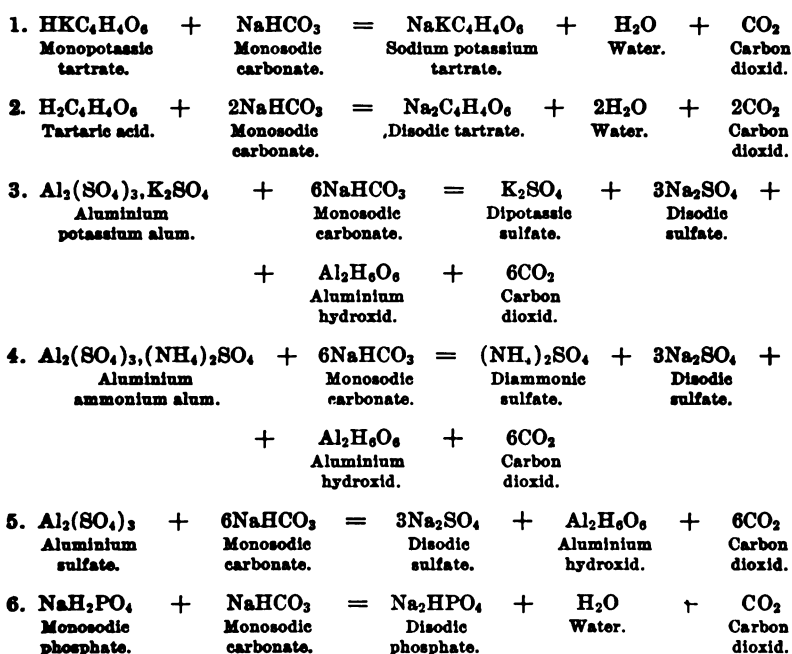
It crystallizes in hard, opaque (translucent when pure), rhombic prisms, which have an acidulous taste, and are very sparingly soluble in H_2O , still less soluble in alcohol. Its solution is acid, and dissolves many metallic oxids with formation of double tartrates. When boiled with antimony trioxid, it forms tartar emetic.

It is used in the household, combined with monosodic carbonate,

in baking, the two substances reacting upon each other to form Rochelle salt, with liberation of carbon dioxid.

Baking Powders are now largely used as substitutes for yeast to "raise" biscuits, cakes, etc. Their action is based upon the decomposition of HNaCO_3 by some salt having an acid reaction, or by a weak acid. In addition to the bicarbonate and flour, or cornstarch (added to render the bulk convenient to handle and to diminish the rapidity of the reaction), they contain cream of tartar, tartaric acid, alum, or acid phosphates. Sometimes ammonium sesquicarbonate is used, in whole or in part, in place of sodium carbonate.

The reactions by which the CO_2 is liberated are:



Sodium Potassium Tartrate—Rochelle salt—*Sel de seignette*—*Potassii et sodii tartras* (U. S.)—*Soda tartarata* (Br.)— $\text{NaKC}_4\text{H}_4\text{O}_6 + 4\text{Aq}$ —210+72—is prepared by saturating monopotassic tartrate with disodic carbonate. It crystallizes in large, transparent prisms, which effloresce superficially in dry air and attract moisture in damp air. It fuses at $70^\circ\text{--}80^\circ$ ($158\text{--}176^\circ\text{F.}$), and loses 3Aq at 100° (212°F.). It is soluble in 1.4 parts of cold H_2O .

Potassium Antimonyl Tartrate—*Tartarated antimony*—*Tartar emetic*—*Antimonil et potassii tartras* (U. S.)—*Antimonium tartaratum* (Br.)— $(\text{SbO})\text{KC}_4\text{H}_4\text{O}_6 + \frac{1}{2}\text{Aq}$ —331.6—is prepared by boil-

ing a mixture of 3 pts. Sb_2O_3 and 4 pts. $\text{H}_2\text{C}_2\text{O}_4$ in H_2O for an hour, filtering, and allowing to crystallize. When required pure, it must be made from pure materials.

It crystallizes in transparent, soluble, right rhombic octahedra, which turn white in air. Its solutions are acid in reaction, have a nauseating metallic taste, and are precipitated by alcohol. The crystals contain $\frac{1}{2}$ Aq, which they lose entirely at 100° (212° F.), and, partially, by exposure to air. It is decomposed by the alkalis, alkaline earths, and alkaline carbonates, with precipitation of Sb_2O_3 . The precipitate is redissolved by excess of soda or potash, or by tartaric acid. HCl , H_2SO_4 and HNO_3 precipitate corresponding antimonyl compounds from solutions of tartar emetic. It converts mercuric into mercurous chlorid. It forms double tartrates with the tartrates of the alkaloids.

Potassium Cyanid—*Potassii cyanidum* (U. S.)— KCN —65—is obtained by heating a mixture of potassium ferrocyanid and dry K_2CO_3 , as long as effervescence continues; decanting and crystallizing.

It is usually met with in dull, white, amorphous masses. Odorless when dry; it has the odor of hydrocyanic acid when moist. It is deliquescent, and very soluble in H_2O ; almost insoluble in alcohol. Its solution is acrid and bitter in taste, with an after-taste of hydrocyanic acid. It is very readily oxidized to the cyanate, a property which renders it valuable as a reducing agent. Solutions of KCN dissolve I , AgCl , the cyanids of Ag and Au , and many metallic oxides.

It is actively poisonous, and produces its effects by decomposition and liberation of hydrocyanic acid (*q. v.*).

Potassium Ferrocyanid—*Yellow prussiate of potash*—*Potassii ferrocyanidum* (U. S.); *Potassæ prussias flava* (Br.)— $\text{K}_4[\text{Fe}(\text{CN})_6] + 3 \text{ Aq}$ —367.9+54.—This salt, the source of the other cyanogen compounds, is manufactured by adding nitrogenous organic matter (blood, bones, hoofs, leather, etc.) and iron to K_2CO_3 in fusion; or by other processes in which the N is obtained from the residues of the purification of coal gas, from atmospheric air, or from ammoniacal compounds.

It forms soft, flexible, lemon-yellow crystals, permanent in air at ordinary temperatures. They begin to lose Aq at 60° (140° F.), and become anhydrous at 100° (212° F.). Soluble in H_2O ; insoluble in alcohol, which precipitates it from its aqueous solution. When calcined with KHO or K_2CO_3 , potassium cyanid and cyanate are formed, and Fe is precipitated. Heated with dilute H_2SO_4 , it yields an insoluble white or blue salt, potassium sulfate, and hydrocyanic acid. Its solutions form, with those of many of the metallic salts, insoluble ferrocyanids; those of Zn , Pb , and Ag are white, cupric ferrocyanid

is mahogany-colored, ferrous ferrocyanid is bluish white, ferric ferrocyanid, Prussian blue, is dark blue. Blue ink is a solution of Prussian blue in a solution of oxalic acid.

Potassium Ferricyanid—Red prussiate of potash— $K_3Fe(CN)_6$ —G57.8—is prepared by acting upon the ferrocyanid with chlorine; or, better, by heating the white residue of the action of H_2SO_4 upon potassium ferrocyanid, in the preparation of hydrocyanic acid, with a mixture of 1 vol. HNO_3 and 20 vols. H_2O ; the blue product is digested with H_2O , and potassium ferrocyanid, the solution filtered and evaporated. It forms red, oblique rhombic prisms, almost insoluble in alcohol. With solutions of ferrous salts it gives a dark blue precipitate, Turnbull's blue.

Analytical Characters.—(1) Platinic chlorid, in presence of HCl : yellow ppt., K_2PtCl_6 ; crystalline if slowly formed; sparingly soluble in H_2O , much less so in alcohol. (2) Tartaric acid in not too dilute solution: white ppt.; soluble in alkalies and in concentrated acids. (3) Hydrofluosilicic acid: translucent, gelatinous ppt.; forms slowly; soluble in strong alkalies. (4) Perchloric acid: white ppt.; sparingly soluble in H_2O ; insoluble in alcohol. (5) Phosphomolybdic acid: white ppt.; forms slowly. (6) Colors the Bunsen flame violet (the color is only observable through blue glass in the presence of Na), and exhibits a spectrum of two bright lines: $\lambda = 7860$ and 4045 (Fig. 14, No. 3, p. 35).

Action of the Sodium and Potassium Compounds on the Economy.—The hydroxids of Na and K , and in a less degree the carbonates, disintegrate animal tissues, dead or living, with which they come in contact, and, by virtue of this action, act as powerful caustics upon a living tissue. Upon the skin, they produce a soapy feeling, and in the mouth a soapy taste. Like the acids, they cause death, either immediately, by corrosion or perforation of the stomach; or, secondarily, after weeks or months, by closure of one or both openings of the stomach, due to thickening, consequent upon inflammation.

The treatment consists in the neutralization of the alkali by an acid, dilute vinegar. Neutral oils and milk are of service; more by reason of their emollient action than for any power they have to neutralize the alkali, by the formation of a soap, at the temperature of the body.

The other compounds of Na , if the acid be not poisonous, are without deleterious action, unless taken in excessive quantity. Common salt has produced paralysis and death in a dose of half a pound. The neutral salts of K , on the contrary, are by no means without true poisonous action when taken internally, or injected subcutaneously, in sufficient quantities; causing dyspnoea, convulsions, arrest of the

heart's action, and death. In the adult human subject, death has followed the ingestion of doses of 15-30 gms. of the nitrate, in several instances; doses of 8-60 gms. of the sulfate have also proved fatal.

Cesium—*Symbol*=Cs—*Atomic weight*=133; and **Rubidium**—*Symbol*=Rb—*Atomic weight*=85.4—are two rare elements, discovered in 1860 by Kirchoff and Bunsen while examining spectroscopically the ash of a spring water. They exist in very small quantity in *lepidolite*. They combine with O and decompose H_2O even more energetically than does K, forming strongly alkaline hydroxids.

SILVER.

Symbol=Ag(*Argentum*)—*Atomic weight*=108 (O=16:107.93; H=1:107.07)—*Molecular weight*=216 (?)—*Sp. gr.*=10.4-10.54—*Fuses at* 1,000° (1,832° F.).

Although silver is usually classed with the "noble metals," it differs from Au and Pt widely in its chemical characters, in which it more closely resembles the alkaline metals.

When pure Ag is required, coin silver is dissolved in HNO_3 and the diluted solution precipitated with HCl. The silver chlorid is washed, until the washings no longer precipitate with silver nitrate; and reduced, either (1) by suspending it in dilute H_2SO_4 in a platinum basin, with a bar of pure Zn, and washing thoroughly, after complete reduction; or (2) by mixing it with chalk and charcoal (AgCl, 100 parts; C, 5 parts; $CaCO_3$, 70 parts), and gradually introducing the mixture into a red-hot crucible.

Silver is a white metal; very malleable and ductile; the best known conductor of heat and electricity. It is not acted on by pure air, but is blackened in air containing a trace of H_2S . It combines directly with Cl, Br, I, S, P, and As. Hot H_2SO_4 dissolves it as sulfate, and HNO_3 as nitrate. The caustic alkalies do not affect it. It alloys readily with many metals; its alloy with Cu is harder than the pure metal.

Silver seems to exist in a number of allotropic modifications, besides that in which it is ordinarily met with. In one of these it is brilliant, metallic, bluish green in color, and dissolves in H_2O , forming a deep red solution; in another it has the color of burnished gold, when dry; and in still another it has also a bluish green color, but is insoluble in water. Very dilute mineral acids immediately convert these modifications into normal gray silver, without evolution of any gas.

Oxids.—Three oxids of silver are known: Ag_2O , Ag_2O , and Ag_2O_2 .

Silver Monoxid—Protoxid—Argenti oxidum—(U. S. ; Br.)—**Ag₂O**—231.8—formed by precipitating a solution of silver nitrate with potash. It is a brownish powder ; faintly alkaline and very slightly soluble in H₂O ; strongly basic. It readily gives up its oxygen. On contact with ammonium hydroxid it forms a fulminating powder.

Silver Chlorid—AgCl—143.4—formed when HCl or a chlorid is added to a solution containing silver. It is white ; turns violet and black in sunlight ; volatilizes at 260° (500° F.) ; sparingly soluble in HCl ; soluble in solutions of the alkaline chlorids, thiosulfates, and cyanids, and in ammonium hydroxid. It crystallizes in octahedra on exposure of its ammoniacal solution.

Silver Bromid—AgBr—and **Iodid—AgI**—are yellowish precipitates, formed by decomposing silver nitrate with potassium bromid and iodid. The former is very sparingly soluble in ammonium hydroxid, the latter is insoluble.

Silver Nitrate—Argenti nitras (U. S. ; Br.)—**AgNO₃**—169.9—is prepared by dissolving Ag in HNO₃, evaporating, fusing, and recrystallizing. It crystallizes in anhydrous, right rhombic plates ; soluble in H₂O. The solutions are colorless and neutral. In the presence of organic matter it turns black in sunlight.

The salt, fused and cast into cylindrical moulds, constitutes **lunar caustic, lapis infernalis ; argenti nitras fusa** (U. S.). If, during fusion, the temperature be raised too high, it is converted into nitrite, O, and Ag ; and if sufficiently heated leaves pure Ag.

Dry Cl and I decompose it, with liberation of anhydrous HNO₃. It absorbs NH₃, to form a white solid, AgNO₃, 3NH₃, which gives up its NH₃ when heated. Its solution is decomposed very slowly by H, with deposition of Ag.

Silver Cyanid—Argenti cyanidum—(U. S.)—**AgCN**—133.9—is prepared by adding KCN or HCN to a solution of AgNO₃. It is a white, tasteless powder ; gradually turns brown in daylight ; insoluble in dilute acids ; soluble in ammonium hydroxid, and in solutions of ammoniacal salts, cyanids, or thiosulfates. The strong mineral acids decompose it with liberation of HCN.

Analytical Characters.—(1) Hydrochloric acid: white flocculent ppt. ; soluble in NH₄HO ; insoluble in HNO₃. (2) Potash or soda: brown ppt. ; insoluble in excess ; soluble in NH₄HO. (3) Ammonium hydroxid, from neutral solutions: brown ppt. ; soluble in excess. (4) Hydrogen sulfid or ammonium sulfhydrate: black ppt. ; insoluble in NH₄HS. (5) Potassium bromid: yellowish white ppt. ; insoluble in acids, if not in great excess ; soluble in NH₄HO. (6) Potassium iodid ; same as KBr, but the ppt. is less soluble in NH₄HO.

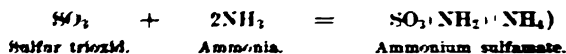
Action on the Economy.—Silver nitrate acts both locally as a

corrosive, and systemically as a true poison. Its local action is due to its decomposition, by contact with organic substances, resulting in the separation of elementary I_2 , whose deposition causes a black stain, and liberation of free HNO_3 , which acts as a caustic. When absorbed, it causes nervous symptoms, referable to its poisonous action. The blue coloration of the skin, observed in those to whom it is administered for some time, is due to the reduction of the metal, under the combined influence of light and organic matter, especially of the latter, as the darkening is observed, although it is less intense, in internal organs.

In acute poisoning by silver nitrate, sodium chlorid or white of egg should be given; and, if the case be seen before the symptoms of corrosion are far advanced, emetics.

AMMONIUM COMPOUNDS.

The Ammonium Theory.—Although the radical ammonium, NH_4 , has probably never been isolated, its existence in the ammoniacal compounds is almost universally admitted. The ammonium hypothesis is based chiefly upon the following facts: (1) the close resemblance of the ammoniacal salts to those of K and Na; (2) when ammonia gas and an acid gas come together, they unite, *without liberation of hydrogen*, to form an ammoniacal salt; (3) the diatomic anhydride unite directly with dry ammonia with formation of the ammonium salt of an amido acid:



(4) when solutions of the ammoniacal salts are subjected to electrolysis, a mixture, having the composition $NH_3 + H$ is given off at the negative pole; (5) amalgam of sodium, in contact with a concentrated solution of ammonium chlorid, increases much in volume, and is converted into a light, soft mass, having the luster of mercury. This ammonium amalgam is decomposed gradually, giving off ammonia and hydrogen in the proportion $NH_3 + H$; (6) if the gases $NH_3 + H$, given off by decomposition of the amalgam, exist there in simple solution, the liberated H would have the ordinary properties of that element. If, on the other hand, they exist in combination, the H would exhibit the more energetic affinities of an element in the nascent state. The hydrogen so liberated is in the nascent state.

Ammonium Hydroxid—*Caustic ammonia*— NH_4HO —35—has never been isolated, probably owing to its tendency to decomposition; $NH_4HO = NH_3 + H_2O$. It is considered as existing in the so-called aqueous solutions of ammonia. These are colorless liquids; of less

sp. gr. than H_2O ; strongly alkaline; and having the taste and odor of ammonia, which gas they give off on exposure to air, and more rapidly when heated. They are neutralized by acids, with elevation of temperature and formation of ammoniacal salts. The **Aqua ammoniæ** (U. S.) and **Liq. ammoniæ** (Br.) are such solutions.

Sulfids.—Four are known: $(\text{NH}_4)_2\text{S}$, $(\text{NH}_4)_2\text{S}_2$, $(\text{NH}_4)_2\text{S}_4$, and $(\text{NH}_4)_2\text{S}_5$; as well as a sulfhydrate $(\text{NH}_4)\text{HS}$.

Ammonium Sulfhydrate— NH_4HS —51—is formed, in solution, by saturating a solution of NH_4HO with H_2S ; or, anhydrous, by mixing equal volumes of dry NH_3 and dry H_2S .

The anhydrous compound is a colorless, transparent, volatile and soluble solid. The solution, when freshly prepared, is colorless, but soon becomes yellow from oxidation, and formation of ammonium disulfid and thiosulfate, and finally deposits sulfur.

The sulfids and hydrosulfid of ammonium are also formed during the decomposition of protein bodies, and exist in the gases formed in burial vaults, sewers, etc.

Ammonium Chlorid—**Sal ammoniac**—**Ammonii chloridum** (U. S.; Br.)— NH_4Cl —53.5—is obtained from the ammoniacal water of gas works. It is a translucent, fibrous, elastic solid; salty in taste, neutral in reaction; volatile without fusion or decomposition; soluble in H_2O . Its solution is neutral, but loses NH_3 and becomes acid when boiled.

Ammonium chlorid exists in small quantity in the gastric juice of the sheep and dog; also in the perspiration, urine, saliva and tears.

Ammonium Bromid—**Ammonii bromidum** (U. S.)— $(\text{NH}_4)\text{Br}$ —98—is formed either by combining NH_3 and HBr ; by decomposing ferrous bromid with NH_4HO ; or by double decomposition between KBr and $(\text{NH}_4)_2\text{SO}_4$. It is a white, granular powder, or crystallizes in large prisms, which turn yellow on exposure to air; quite soluble in H_2O ; volatile without decomposition.

Ammonium Iodid—**Ammonii iodidum** (U. S.)— NH_4I —145—is formed by union of equal volumes of NH_3 and HI ; or by double decomposition of KI and $(\text{NH}_4)_2\text{SO}_4$. It crystallizes in deliquescent, very soluble cubes.

Ammonium Nitrate—**Ammonii nitras**—(U. S.)— $(\text{NH}_4)\text{NO}_3$ —80—is prepared by neutralizing HNO_3 with ammonium hydroxid or carbonate. It crystallizes in flexible, anhydrous, six-sided prisms; very soluble in H_2O , with considerable diminution of temperature; fuses at 150° (302°F.), and decomposes at 210° (410°F.), with formation of nitrous oxid: $(\text{NH}_4)\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$. If the heat be suddenly applied, or allowed to surpass 250° (482°F.), NH_3 , NO , and N_2O are formed. When fused it is an active oxidant.

Sulfates.—**Diammonic Sulfate**—*Ammonic sulfate*—**Ammonii**

sulfas (U. S.)— $(\text{NH}_4)_2\text{SO}_4$ —132—is obtained by collecting the distillate from a mixture of ammoniacal gas liquor and lime in H_2SO_4 . It forms anhydrous, soluble, rhombic crystals; fuses at 140° (284° F.), and is decomposed at 200° (392° F.) into NH_3 and $\text{H}(\text{NH}_4)\text{SO}_4$.

Monoammonic Sulfate—*Hydroammonic sulfate*—*Bisulfate of ammonia*— $\text{H}(\text{NH}_4)\text{SO}_4$ —115—is formed by the action of H_2SO_4 on $(\text{NH}_4)_2\text{SO}_4$. It crystallizes in right rhombic prisms, soluble in H_2O and in alcohol.

Ammonium Acetate— $(\text{NH}_4)\text{C}_2\text{H}_3\text{O}_2$ —77—is formed by saturating acetic acid with NH_3 , or with ammonium carbonate. It is a white, odorless, very soluble solid; fuses at 86° (186.8° F.), and gives off NH_3 ; then acetic acid, and finally acetamid. **Liq. ammonii acetatis** = **Spirit of Mindererus** is an aqueous solution of this salt.

Carbonates.—**Diammonic Carbonate**—*Ammonic carbonate*—*Neutral ammonium carbonate*— $(\text{NH}_4)_2\text{CO}_3 + \text{Aq}$ —96+18—has been obtained as a white crystalline solid. In air it is rapidly decomposed into NH_3 and $\text{H}(\text{NH}_4)\text{CO}_3$.

Monoammonic Carbonate—*Hydroammonic carbonate*—*Acid carbonate of ammonia*— $\text{H}(\text{NH}_4)\text{CO}_3$ —79—is prepared by saturating a solution of NH_4HO or ammonium sesquicarbonate with CO_2 . It crystallizes in large, rhombic prisms; quite soluble in H_2O . At 60° (140° F.) it is decomposed into NH_3 and CO_2 .

Ammonium Sesquicarbonate—**Sal volatile**—**Preston salts**—**Ammonii carbonas** (U. S.); **Ammoniaë carbonas** (Br.)— $\text{NH}_4\text{HCO}_3 + \text{NH}_4\text{CO}_2\text{NH}_2$ —157—is prepared by heating a mixture of NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ and chalk, and condensing the product. It crystallizes in rhombic prisms; has an ammoniacal odor and an alkaline reaction; soluble in H_2O . By exposure to air or by heating its solution, it is decomposed into H_2O , NH_3 , and $\text{H}(\text{NH}_4)\text{CO}_3$. It is not a pure salt, but a mixture of monoammonic carbonate and ammonium carbamate.

Analytical Characters.—(1) Entirely volatile at high temperatures. (2) Heated with KHO , the ammoniacal compounds give off NH_3 , recognizable: (a) by changing moist red litmus to blue; (b) by its odor; (c) by forming a white cloud on contact with a glass rod moistened with HCl . (3) With platinic chlorid: a yellow, crystalline ppt. (4) With hydrosodic tartrate, in moderately concentrated and neutral solution: a white crystalline ppt.

Action on the Economy.—Solutions of the hydroxid and carbonate act upon animal tissues in the same way as the corresponding Na and K compounds. They, moreover, disengage NH_3 , which causes intense dyspnœa, irritation of the air-passages, and suffocation.

The treatment indicated is the neutralization of the alkali by a dilute acid. Usually the vapor of acetic acid or of dilute HCl must be administered by inhalation.

II. THALLIUM GROUP.

THALLIUM.

Symbol=Tl—*Atomic weight*=204 (O=16:204.1; H=1:202.48)—*Sp. gr.*=11.8–11.9—*Fuses at* 294° (561° F.)—*Discovered by Crookes* (1861).

A rare element, first obtained from the deposits in flues of sulfuric acid factories, in which pyrites from the Hartz were used. It resembles Pb in appearance and in physical properties, but differs entirely from that element in its chemical characters. It resembles Au in being univalent and trivalent, but differs from it, and resembles the alkali metals in being readily oxidized, in forming alums, and in forming no acid hydrate. It differs from the alkali metals in the thallic compounds, which contain Tl'''. It is characterized spectroscopically by a bright green line— $\lambda=5349$.

III. CALCIUM GROUP.

Metals of the Alkaline Earths.

CALCIUM—STRONTIUM—BARIUM.

The members of this group are bivalent in all their compounds; each forms two oxids: MO and MO₂; each forms a hydroxid, having well-marked basic characters.

CALCIUM.

Symbol=Ca—*Atomic weight*=40 (O=16:40; H=1:39.68)—*Molecular weight*=80 (!)—*Sp. gr.*=1.984—*Discovered by Davy in* 1808—*Name from calx*=lime.

Occurs only in combination, as limestone, marble, chalk (CaCO₃), gypsum, selenite, alabaster (CaSO₄), and many other minerals. In bones, egg-shells, oyster-shells, etc., as Ca₃(PO₄)₂ and CaCO₃, and in many vegetable structures.

The element is obtained by electrolysis of fused CaCl₂, or by heating CaI₂ with Na. It is a hard, yellow, very ductile, and malleable metal; fusible at a red heat; not sensibly volatile. In dry air it is not altered, but is converted into CaH₂O₂ in damp air; decomposes H₂O; burns when heated in air.

Calcium Monoxid—**Quick Lime**—**Lime**—**Calx** (U. S.; Br.)—CaO—56—is prepared by heating a native carbonate (limestone); or,

when required pure, by heating a carbonate, prepared by precipitation.

It occurs in white or grayish, amorphous masses; odorless; alkaline, caustic; almost infusible; sp. gr. 2.3. With H_2O it gives off great heat and is converted into the hydroxid (slaking). In air it becomes **air-slaked**, falling into a white powder, having the composition $CaCO_3, CaH_2O_2$.

Calcium Hydroxid—Slaked lime—Calcis hydras (Br.)— CaH_2O_2 —74—is formed by the action of H_2O on CaO . If the quantity of H_2O used be one-third that of the oxid, the hydroxid remains as a dry, white, odorless powder; alkaline in taste and reaction; more soluble in cold than in hot H_2O . If the quantity of H_2O be greater, a creamy or milky liquid remains, **cream**, or **milk of lime**; a solution holding an excess in suspension. With a sufficient quantity of H_2O the hydroxid is dissolved to a clear solution, which is **lime water**—**Liquor calcis** (U. S.; Br.). The solubility of CaH_2O_2 is diminished by the presence of alkalies, and is increased by sugar or mannite; **Liq. calc. saccharatus** (Br.); **Syrupus calcis** (U. S.). Solutions of CaH_2O_2 absorb CO_2 with formation of a white deposit of $CaCO_3$.

Calcium Carbid— CaC_2 —is formed by the action of a very high temperature upon a mixture of quick lime and carbon. It is an amorphous grayish substance, which is decomposed by water, yielding acetylene gas: $CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$. One kilo. CaC_2 yields 440 litres C_2H_2 .

Calcium Chlorid—Calcii chloridum (U. S.; Br.)— $CaCl_2$ —111—is obtained by dissolving marble in HCl : $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$. It is bitter, deliquescent, very soluble in H_2O ; crystallizes with 6Aq, which it loses when fused, leaving a white, amorphous mass, used as a drying agent.

Chloride of Lime—Bleaching powder—Calx chlorata (U. S.; Br.)—is a white or yellowish, hygroscopic powder, prepared by passing Cl over CaH_2O_2 , maintained in excess. It is bitter and acid in taste; soluble in cold H_2O ; decomposed by boiling H_2O , and by the weakest acids, with liberation of Cl . It is decomposed by CO_2 , with formation of $CaCO_3$, and liberation of hypochlorous acid, if it be moist; or of Cl , if it be dry. A valuable disinfectant. The "available chlorin" is the amount liberated by acids, and should exceed 35%.

Bleaching powder was formerly considered as a mixture of calcium chlorid and hypochlorite, formed by the reaction: $2CaO + 2Cl_2 = CaCl_2 + Ca(ClO)_2$, but it is more probable that it is a definite compound having the formula $CaCl(OCl)$, which is decomposed by H_2O into a mixture of $CaCl_2$ and $Ca(ClO)_2$; and by dilute HNO_3 or H_2SO_4 with formation of $HClO$.

Calcium Sulfate— CaSO_4 —136—occurs in nature as *anhydrite*; and with 2Aq in *gypsum*, *alabaster*, *selenite*; and in solution in natural waters. *Terra alba* is ground gypsum. It crystallizes with 2Aq in right rhombic prisms; sparingly soluble in H_2O , more soluble in H_2O containing free acids or chlorids. When the hydrated salt (gypsum) is heated to 80° (176°F.), or, more rapidly, between 120° – 130° (248° – 266°F.), it loses its Aq and is converted into a white, opaque mass, which, when ground, is **plaster of Paris**.

The **setting** of plaster when mixed with H_2O , is due to the conversion of the anhydrous into the crystalline, hydrated salt. The ordinary plastering should never be used in hospitals, as, by reason of its irregularities and porosity, it soon becomes saturated with septic germs, and cannot be thoroughly purified by disinfectants. Plaster surfaces may, however, be rendered dense, and be highly polished, so as to be smooth and impermeable, by adding glue and alum, or an alkaline silicate to the water used in mixing.

Phosphates.—Three are known: $\text{Ca}_3(\text{PO}_4)_2$; $\text{Ca}_2(\text{HPO}_4)_2$, and $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

Tricalcic Phosphate—*Tribasic or neutral phosphate*—**Bone phosphate**—**Calcii phosphas præcipitatus** (U. S.)—**Calcis phosphas** (Br.)— $\text{Ca}_3(\text{PO}_4)_2$ —310—occurs in nature, in soils, guano, *coprolites*, phosphorite, in all plants, and in every animal tissue and fluid. It is obtained by dissolving bone-ash in HCl , filtering, and precipitating with NH_4HO ; or by double decomposition between CaCl_2 and an alkaline phosphate. When freshly precipitated it is gelatinous; when dry, a light, white, amorphous powder; almost insoluble in pure H_2O ; soluble to a slight extent in H_2O containing ammoniacal salts, or NaCl or NaNO_3 ; readily soluble in dilute acids, even in H_2O charged with carbonic acid. It is decomposed by H_2SO_4 into CaSO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2$. **Bone-ash** is an impure form of $\text{Ca}_3(\text{PO}_4)_2$, obtained by calcining bones, and used in the manufacture of P and of superphosphate.

Dicalcic Phosphate— $\text{Ca}_2(\text{HPO}_4)_2 + 2\text{Aq}$ —272+36—is a crystalline, insoluble salt; formed by double decomposition between CaCl_2 and HNa_2PO_4 in acid solution.

Monocalcic Phosphate—*Acid calcium phosphate*—**Superphosphate of lime**— $\text{Ca}(\text{H}_2\text{PO}_4)_2$ —234—exists in brain tissue, and in those animal liquids whose reaction is acid. It is also formed when $\text{Ca}_3(\text{PO}_4)_2$ is dissolved in an acid, and is manufactured for use as a manure, by decomposing bone-ash with H_2SO_4 . It crystallizes in pearly plates; very soluble in H_2O . Its solutions are acid.

Calcium Carbonate— CaCO_3 —100—the most abundant of the natural compounds of Ca, exists as *limestone*, *calcspar*, *chalk*, *marble*, *Iceland spar*, and *aragonite*; and forms the basis of corals, shells of

crustacea and of molluscs, etc. **Otoliths**, which occur in the internal ear, parotid calculi, and sometimes vesical calculi consist of CaCO_3 .

Precipitated chalk—*Calcii carbonas præcipitata* (U. S. ; Br.)—is prepared by precipitating a solution of CaCl_2 with one of Na_2CO_3 . **Prepared chalk**—*Creta præparata* (U. S. ; Br.)—is native chalk, purified by grinding with H_2O , diluting, allowing the coarser particles to subside, decanting the still turbid liquid, collecting and drying the finer particles. A process known as **elutriation** or **levigation**.

It is a white powder, almost insoluble in pure H_2O ; much more soluble in H_2O containing carbonic acid, the solution being regarded as containing **monocalcic carbonate** $\text{H}_2\text{Ca}(\text{CO}_3)_2$. At a red heat it yields CO_2 and CaO . It is decomposed by acids with liberation of CO_2 .

Calcium Oxalate—*Oxalate of lime*— CaC_2O_4 —128—exists in the sap of many plants, in human urine, and in **mulberry calculi**, and is formed as a white, crystalline precipitate, by double decomposition, between a Ca salt and an alkaline oxalate. It is insoluble in H_2O , acetic acid, or NH_4HO ; soluble in the mineral acids and in solution of H_2NaPO_4 .

Analytical Characters.—(1) Ammonium sulfhydrate: nothing, unless the Ca salt be the phosphate, oxalate or fluorid, when it forms a white ppt. (2) Alkaline carbonates: white ppt.; not prevented by the presence of ammoniacal salts. (3) Ammonium oxalate: white ppt., insoluble in acetic acid; soluble in HCl or HNO_3 . (4) Sulfuric acid: white ppt., either immediately or on dilution with three volumes of alcohol; very sparingly soluble in H_2O , insoluble in alcohol; soluble in sodium thiosulfate solution. (5) Sodium tungstate: dense white ppt., even from dilute solutions. (6) Colors the flame of the Bunsen burner reddish-yellow, and exhibits a spectrum of a number of bright bands, the most prominent of which are: $\lambda=6265, 6202, 6181, 6044, 5982, 5933, 5543, \text{ and } 5517$.

STRONTIUM.

Symbol=Sr—*Atomic weight*=87.5 (O=16.86.9; H=1.87.6)—*Sp. gr.*=2.54.

An element, not as abundant as Ba, occurring principally in the minerals *strontianite* (SrCO_3) and *celestine* (SrSO_4). Its compounds resemble those of Ca and Ba. Its nitrate is used in making red fire. The iodid and the lactate are used in medicine.

Analytical Characters.—(1) Behaves like Ba with alkaline carbonates and Na_2HPO_4 . (2) Calcium sulfate: a white ppt., which forms slowly; accelerated by addition of alcohol. (3) The Sr com-

pounds color the Bunsen flame red, or, as observed through blue glass, purple or rose color. The Sr flame gives a spectrum of many bands, of which the most prominent are: $\lambda=6694, 6664, 6059, 6031, 4607$.

BARIUM.

Symbol=Ba—*Atomic weight*=137.5 (O=16:137.4; H=1:136.3)—*Molecular weight*=273.6 (?)—*Sp. gr.*=4.0—Discovered by Davy, 1808—Name from βαρύς=heavy.

Occurs only in combination, principally as *heavy spar* (BaSO_4) and *witherite* (BaCO_3). It is a pale yellow, malleable metal, quickly oxidized in air, and decomposing H_2O at ordinary temperatures.

Oxids.—**Barium Monoxid**—**Baryta**— BaO —153.4—is prepared by calcining the nitrate. It is a grayish-white or white, amorphous, caustic solid. In air it absorbs moisture and CO_2 , and combines with H_2O as does CaO .

Barium Dioxid—*Barium peroxid*— BaO_2 —169.4—is prepared by heating the monoxid in O. It is a grayish-white, amorphous solid. Heated in air it is decomposed: $\text{BaO}_2=\text{BaO}+\text{O}$. Aqueous acids dissolve it with formation of a barytic salt and H_2O_2 .

Barium Hydroxid— BaH_2O_2 —171.5—is prepared by the action of H_2O on BaO . It is a white, amorphous solid, soluble in H_2O . Its aqueous solution, **baryta water**, is alkaline, and absorbs CO_2 , with formation of a white deposit of BaCO_3 .

Barium Chlorid— $\text{BaCl}_2+2 \text{ Aq}$ —208.3+36—is obtained by treating BaS or BaCO_3 with HCl . It crystallizes in prismatic plates, permanent in air, soluble in H_2O .

Barium Nitrate— $\text{Ba}(\text{NO}_3)_2$ —261.4—is prepared by neutralizing HNO_3 with BaCO_3 . It forms octahedral crystals, soluble in H_2O .

Barium Sulfate— BaSO_4 —233.4—occurs in nature as *heavy spar*, and is formed as an amorphous, white powder, insoluble in acids, by double decomposition between a Ba salt and a sulfate in solution. It is insoluble in H_2O and in acids. It is used as a pigment, **permanent white**.

Barium Carbonate— BaCO_3 —197.4—occurs in nature as *witherite*, and is formed by double decomposition between a Ba salt and a carbonate in alkaline solution. It is a heavy, amorphous, white powder, insoluble in H_2O , soluble with effervescence in acids.

Analytical Characters.—(1) Alkaline carbonates: white ppt., in alkaline solution. (2) Sulfuric acid, or calcium sulfate: white ppt., insoluble in acids. (3) Sodium phosphate: white ppt., soluble in HNO_3 . (4) Colors the Bunsen flame greenish-yellow, and exhibits a spectrum of several lines, the most prominent of which are: $\lambda=6108, 6044, 5881, 5536$.

Action on the Economy.—The oxids and hydroxid act as corrosives, by virtue of their alkalinity, and also as true poisons. All soluble compounds of Ba, and those which are readily converted into soluble compounds in the stomach, are actively poisonous. Soluble sulfids, followed by emetics, are indicated as antidotes. The sulfate, notwithstanding its insolubility in water, is poisonous to some animals.

IV. MAGNESIUM GROUP.

MAGNESIUM—ZINC—CADMIUM.

Each of these elements forms a single oxid—a corresponding basic hydroxid, and a series of salts in which its atoms are bivalent.

The existence of potassium zincate, ZnO_2K_2 , obtainable by the action of zinc hydroxid and potassium hydroxid upon each other: $\text{Zn}(\text{OH})_2 + 2\text{KHO} = \text{ZnO}_2\text{K}_2 + 2\text{H}_2\text{O}$ would seem to require the transferral of zinc to the amphoteric class; the $\text{Zn}(\text{OH})_2$ in the above reaction fulfilling the requirements of the second definition of acids (see p. 63). Potassium zincate should, however, be considered rather as a double oxid of zinc and potassium: ZnOK_2O or $\text{Zn}.\text{OK}.\text{OK}$, than as a true salt for the following reasons: (1) It is also produced by the reaction: $\text{Zn} + 2\text{KHO} = \text{ZnO}_2\text{K}_2 + \text{H}_2$, in which, if ZnO_2K_2 be a salt, KHO, the most distinctly basic substance known, must be considered to be an acid. (2) In the electrolysis of ZnO_2K_2 the Zn and K go to the negative pole, and the O to the positive, while in the electrolysis of true ternary salts, such as K_2SO_4 , the oxygen accompanies the other electro-negative element to the positive pole, the metal going alone to the negative. Moreover, the zincates are unstable bodies, and the most prominent function of $\text{Zn}(\text{OH})_2$ is that of a base, as in the reaction $\text{Zn}(\text{OH})_2 + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + 2\text{HO}_2$. (See Aluminium, p. 245).

MAGNESIUM.

Symbol=Mg—*Atomic weight*=24 (O=16:24.36; H=1:24.17)—*Molecular weight*=48 (?)—*Sp. gr.*=1.75—Fuses at 1000° (1832° F.)—*Discovered by Davy*, 1808.

Occurs as carbonate in *dolomite* or *magnesian limestone*, and as silicate in *mica*, *asbestos*, *soapstone*, *meerschaum*, *talc*, and in other minerals. It also accompanies Ca in the forms in which it is found in the animal and vegetable worlds.

It is prepared by heating its chlorid with Na, or by electrolysis of the fused chlorid. It is a hard, light, malleable, ductile, white metal. It burns with great brilliancy when heated in air (magnesium light),

but may be distilled in H. The flash light used by photographers is a mixture of powdered Mg with an oxidizing agent, KClO_3 or KNO_3 . It decomposes vapor of H_2O when heated; reduces CO_2 with the aid of heat, and combines directly with Cl, S, P, As and N. It dissolves in dilute acids, but is not affected by alkaline solutions.

Magnesium Oxid—**Calcined magnesia**—**Magnesia** (U. S. ; Br.)— MgO —40—is obtained by calcining the carbonates, hydroxid, or nitrate. It is a light, bulky, tasteless, odorless, amorphous, white powder; alkaline in reaction; almost insoluble in H_2O ; readily soluble without effervescence in acids.

Magnesium Hydroxid— MgH_2O_2 —58—occurs in nature, and is formed when a solution of a Mg salt is precipitated with excess of NaHO , in absence of ammoniacal salts. It is a heavy, white powder, insoluble in H_2O ; absorbs CO_2 .

Magnesium Chlorid— MgCl_2 —95—is formed when MgO or MgCO_3 is dissolved in HCl . It is an exceedingly deliquescent, soluble substance, which is decomposed into HCl and MgO when its aqueous solutions are evaporated to dryness. Like all the soluble Mg compounds it is bitter in taste, and accompanies the sulfate and bicarbonate in the *bitter waters*.

Magnesium Sulfate—**Epsom salt**—*Seidlitz salt*—**Magnesii sulfas** (U. S.)—**Magnesia sulfas** (Br.)— $\text{MgSO}_4 + 7\text{Aq}$ —120+126—exists in solution in sea water and in the waters of many mineral springs, especially those known as *bitter waters*. It is formed by the action of H_2SO_4 on MgCO_3 . It crystallizes in right rhombic prisms; bitter; slightly effervescent, and quite soluble in H_2O . Heated, it fuses and gradually loses 6Aq up to 132° (269.6°F.); the last Aq it loses at 210° (410°F.).

Phosphates.—Resemble those of Ca in their constitution and properties, and accompany them in the situations in which they occur in the animal body, but in much smaller quantity.

Magnesium also forms double phosphates, constituted by the substitution of one atom of the bivalent metal for two of the atoms of basic hydrogen, of a molecule of phosphoric acid, and of an atom of alkaline metal, or of an ammonium group, for the remaining basic hydrogen.

Ammonio-Magnesian Phosphate—**Triple phosphate**— $\text{Mg}(\text{NH}_4)\text{PO}_4 + 6\text{Aq}$ —137+108—is produced when an alkaline phosphate and NH_4HO are added to a solution containing Mg. When heated it is converted into **magnesium pyrophosphate**, $\text{Mg}_2\text{P}_2\text{O}_7$, in which form H_3PO_4 and Mg are usually weighed in quantitative analysis.

Carbonates.—**Magnesium Carbonate**—*Neutral carbonate*— MgCO_3 —84—exists native in *magnesite*, and, combined with CaCO_3 , in *dolomite*. It cannot be formed, like other carbonates, by decomposing

a Mg salt with an alkaline carbonate, but may be obtained by passing CO_2 through H_2O holding tetramagnesian tricarbonatè in suspension.

Trimagnesian Dicarbonatè— $(\text{MgCO}_3)_2\text{MgH}_2\text{O}_2 + 2\text{Aq}$ —226+36—is formed, in small crystals, when a solution of MgSO_4 is precipitated with excess of Na_2CO_3 , and the mixture boiled.

Tetramagnesian Tricarbonatè—**Magnesia alba**—**Magnesian carbonas** (U. S.)—**Magnesiæ carbonas** (Br.)— $(\text{MgCO}_3)_3\text{MgH}_2\text{O}_2 + 3\text{Aq}$ —310+54—occurs in commerce in light, white cubes, composed of a powder which is amorphous, or partly crystalline. It is prepared by precipitating a solution of MgSO_4 with one of Na_2CO_3 . If the precipitation occur in cold, dilute solutions (**Magnesiæ carbonas lœvis**, Br.), very little CO_2 is given off; a light, bulky precipitate falls, and the solution contains magnesium, probably in the form of the bicarbonatè $\text{Mg}(\text{HCO}_3)_2$. This solution, on standing, deposits crystals of the carbonatè, $\text{MgCO}_3 + 3\text{Aq}$. If hot concentrated solutions be used, and the liquid be then boiled upon the precipitate, CO_2 is given off, and a denser, heavier precipitate is formed, which varies in composition, according to the length of time during which the boiling is continued, and to the presence or absence of excess of sodium carbonatè. The pharmaceutical product frequently contains $(\text{MgCO}_3)_4$, $\text{MgH}_2\text{O}_2 + 4\text{H}_2\text{O}$, or even $(\text{MgCO}_3)_2\text{MgH}_2\text{O}_2 + 2\text{H}_2\text{O}$. All of these compounds are very sparingly soluble in H_2O , but much more soluble in H_2O containing ammoniacal salts.

Analytical Characters.—(1) Ammonium hydroxid: voluminous, white ppt. from neutral solutions. (2) Potash or soda: voluminous, white ppt. from warm solutions, prevented by the presence of NH_4 salts, and of certain organic substances. (3) Ammonium carbonatè: slight ppt. from hot solutions; prevented by the presence of NH_4 salts. (4) Sodium or potassium carbonatè: white ppt., best from hot solution; prevented by the presence of NH_4 compounds. (5) Disodic phosphatè: white ppt. in hot, not too dilute solutions. (6) Oxalic acid: nothing alone, but in presence of NH_4HO , a white ppt.; not formed in presence of salts of NH_4 .

ZINC.

Symbol=Zn—**Atomic weight**=65 (O=16:65.4; H=1:64.88)—**Molecular weight**=65—**Sp. gr.**=6.862–7.215—**Fuses at** 415° (779° F.)—**Distills at** 1040° (1904° F.).

Occurs principally in *calamine* (ZnCO_3); and *blende* (ZnS); also as oxid and silicate; never free. It is separated from its ores by calcining, roasting, and distillation.

It is a bluish-white metal; crystalline, granular, or fibrous; quite malleable and ductile when pure. The commercial metal is usually

brittle. At 130° – 150° (266° – 302° F.) it is pliable, and becomes brittle again above 200° – 210° (392° – 410° F.).

At 500° (932° F.) it burns in air, with a greenish-white flame, and gives off snowy-white flakes of the oxid (*lana philosophica; nil album; pompholix*). In moist air it becomes coated with a film of hydrocarbonate. It decomposes steam when heated.

Pure H_2SO_4 and pure Zn do not react together in the cold. If the acid be diluted, however, it dissolves the Zn, with evolution of H, and formation of ZnSO_4 , in the presence of a trace of Pt or Cu. The commercial metal dissolves readily in dilute H_2SO_4 , with evolution of H, and formation of ZnSO_4 , the action being accelerated in presence of Pt, Cu, or As. Zinc surfaces, thoroughly coated with a layer of an amalgam of Hg and Zn, are only attacked by H_2SO_4 if they form part of closed galvanic circuit; hence the zincs of galvanic batteries are protected by *amalgamation*. Zinc also decomposes HNO_3 , HCl , and acetic acid. Zinc dissolves in strong solutions of the caustic alkalies with evolution of hydrogen and formation of double oxids (zincates): $\text{Zn} + 2\text{KHO} = \text{ZnO}_2\text{K}_2 + \text{H}_2$. It also decomposes many metallic salts in solution with deposition of the metal.

When required for toxicological analysis, zinc must be perfectly free from As, and sometimes from P. It is better to test samples until a pure one is found, than to attempt the purification of a contaminated metal.

Zinc surfaces are readily attacked by weak organic acids. Vessels of *galvanized iron* or *sheet zinc* should therefore never be used to contain articles of food or medicines.

Zinc Oxid—*Zinci oxidum* (U. S.; Br.)— ZnO —81.4—is prepared either by calcining the precipitated carbonate, or by burning Zn in a current of air. An impure oxid, known as *tutty*, is deposited in the flues of zinc furnaces, and in those in which brass is fused. When obtained by calcination of the carbonate, it forms a soft, white, tasteless, and odorless powder. When produced by burning the metal, it occurs in light, voluminous, white masses. It is neither fusible, volatile, nor decomposable by heat, and is completely insoluble in neutral solvents. It dissolves in dilute acids, with formation of the corresponding salts.

It is used in the arts as a white pigment in place of lead carbonate, and is not darkened by H_2S .

Zinc Hydroxid— ZnH_2O_2 —99.4—is not formed by union of ZnO and H_2O ; but is produced when a solution of a Zn salt is treated with KHO. Freshly prepared, it is very soluble in alkalies, and in solutions of NH_4 salts.

Zinc Chlorid—*Butter of zinc*—*Zinci chloridum* (U. S.; Br.)— $\text{ZnCl}_2 + \text{Aq}$ —136.3+18—is obtained by dissolving Zn in HCl , or by

heating Zn in Cl. It is a soft, white, very deliquescent, fusible, volatile mass; very soluble in H_2O , somewhat less so in alcohol. Its solution has a burning, metallic taste; destroys vegetable tissues; dissolves silk; and exerts a strong dehydrating action upon organic substances in general.

In dilute solution it is used as a disinfectant and antiseptic (*Burnett's fluid*), as a preservative of wood and as an embalming injection.

Zinc Sulfate—White vitriol—Zinci sulfas (U.S.; Br.)— $ZnSO_4 + nAq = 161.4 + n18$ —is formed when Zn, ZnO, ZnS, or $ZnCO_3$ is dissolved in diluted H_2SO_4 . It crystallizes below 30° (86° F.) with 7 Aq; at 30° (86° F.) with 6 Aq; between 40° – 50° (104° – 122° F.) with 5 Aq; at 0° (32° F.) from concentrated acid solution with 4 Aq. From a boiling solution it is precipitated by concentrated H_2SO_4 with 2 Aq; from a saturated solution at 100° (212° F.) with 1 Aq; and anhydrous, when the salt with 1 Aq is heated to 238° (460° F.).

The salt usually met with is that with 7 Aq, which is in large, colorless, four-sided prisms; efflorescent; very soluble in H_2O , sparingly soluble in weak alcohol. Its solutions have a strong, styptic taste: coagulate albumen when added in moderate quantity, the coagulum dissolving in an excess; and form insoluble precipitates with the tannins.

Carbonates.—Zinc Carbonate— $ZnCO_3$ —125.4—occurs in nature as calamine. If an alkaline carbonate be added to a solution of a Zn salt, the neutral carbonate, as in the case of Mg, is not formed, but an oxycarbonate, $nZnCO_3$, $nZnH_2O_2$ [Zinci carbonas (U. S.; Br.)], whose composition varies with the conditions under which it is formed.

Analytical Characters.—(1) K, Na or NH_4 hydroxid: white ppt., soluble in excess. (2) Carbonate of K or Na: white ppt., in absence of NH_4 salts. (3) Hydrogen sulfid, in neutral solution: white ppt. In presence of an excess of a mineral acid, the formation of this ppt. is prevented, unless sodium acetate be also present. (4) Ammonium sulfhydrate: white ppt., insoluble in excess, in KHO, NH_4HO , or acetic acid; soluble in dilute mineral acids. (5) Ammonium carbonate: white ppt., soluble in excess. (6) Disodic phosphate, in absence of NH_4 salts: white ppt., soluble in acids or alkalis. (7) Potassium ferrocyanid: white ppt., insoluble in HCl.

Action on the Economy.—All the compounds of Zn which are soluble in the digestive fluids behave as true poisons; and solutions of the chlorid (in common use by tinsmiths, and in disinfecting fluids) have also well-marked corrosive properties. When Zn compounds are taken, it is almost invariably by mistake for other substances: the sulfate for Epsom salt, and solutions of the chlorid for various liquids such as gin, fluid magnesia, vinegar, etc.

Metallic zinc is dissolved by solutions containing NaCl, or organi

acids, for which reason articles of food kept in vessels of galvanized iron become contaminated with zinc compounds, and, if eaten, produce more or less intense symptoms of intoxication. For the same reason materials intended for analysis in cases of supposed poisoning, *should never be packed in jars closed by zinc caps.*

CADMIUM.

Symbol=Cd—*Atomic weight*=111.5 (O=16:112.4; H=1:111.5)—*Molecular weight*=111.8—*Sp. gr.*=8.604—*Fuses at* 227.8° (442° F.)—*Boils at* 860° (1580° F.).

A white metal, malleable and ductile at low temperature, brittle when heated; which accompanies Zn in certain of its ores. It resembles zinc in its physical as well as its chemical characters. It is used in certain fusible alloys, and its iodid is used in photography.

Analytical Characters.—Hydrogen sulfid: bright yellow ppt.; insoluble in NH_4HS , and in dilute acids and alkalies, soluble in boiling HNO_3 or HCl .

V. ALUMINIUM GROUP.

BERYLLIUM—ALUMINIUM—SCANDIUM—GALLIUM—INDIUM.

These elements form one series of compounds, corresponding to the ferric, containing the group $(\text{M}_2)^{\text{vi}}$, but no compounds corresponding to the ferrous M'' and the Ni and Co salts are known. Indeed, certain organic compounds, such as aluminium acetylacetonate, $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$, seem to contain single, trivalent atoms of the metal. The existence of the aluminates, such as $\text{K}_2\text{Al}_2\text{O}_4$, would seem to place aluminium in the amphoteric class. These compounds, which are formed by the reactions: $\text{Al}_2(\text{OH})_6 + 2\text{KHO} = \text{K}_2\text{Al}_2\text{O}_4 + 4\text{H}_2\text{O}$, and $\text{Al}_2 + 2\text{KHO} + 2\text{H}_2\text{O} = \text{K}_2\text{Al}_2\text{O}_4 + 3\text{H}_2$, are double oxids rather than salts. They resemble the zincates and what has been said concerning those compounds (see p. 240) applies also to the aluminates.

ALUMINIUM.

Symbol=Al—*Atomic weight*=27 (O=16:27.1; H=1:26.88)—*Molecular weight*=55 (?)—*Sp. gr.*=2.56–2.67—*Fuses at about* 700° (1292° F.)—*Name from* alumen=*alum*—*Discovered by* Wöhler, 1827.

Occurrence.—Exceedingly abundant in the clays as *silicate*. Also in *feldspar*, *mica*, and *garnet*, *topaz*, and *emerald*. As a fluorid in *cryolite*, and as a hydroxid in *beauxite*.

Preparation.—(1) By decomposing vapor of aluminium chlorid by Na or K (Wöhler). (2) Aluminium hydroxid, mixed with sodium chlorid and charcoal, is heated in Cl, by which a double chlorid of Na and Al ($\text{Na}_2\text{Al}_2\text{Cl}_6$) is formed. This is then heated with Na, when Al and NaCl are produced. (3) These "chemical methods" have been replaced, in the industrial preparation of aluminium, by the electrolytic method, in which a mixture of cryolite and beauxite is treated in an electric furnace.

Properties.—*Physical.*—A bluish-white metal; hard; quite malleable, and ductile, when annealed from time to time; slightly magnetic; a good conductor of electricity; non-volatile; very light, and exceedingly sonorous.

Chemical.—It is not affected by air or O, except at very high temperatures, and then only superficially. If, however, it contain Si, it burns readily in air, forming aluminium silicate. It does not decompose H_2O at a red heat; but in contact with Cu, Pt, or I, it does so at 100° (212° F.). It combines directly with B, Si, Cl, Br, and I. It is attacked by HCl, gaseous or in solution, with evolution of H, and formation of Al_2Cl_6 . It dissolves in alkaline solutions, with formation of aluminates, and liberation of H. It alloys with Cu to form a golden yellow metal (aluminium bronze).

Aluminium Oxid—*Alumina*— Al_2O_3 —102.2—occurs in nature, nearly pure, as *corundum*, *emery*, *ruby*, *sapphire*, and *topaz*; and is formed artificially, by calcining the hydrate, or ammonia alum, at a red heat.

It is a light, white, odorless, tasteless powder; fuses with difficulty; and, on cooling, solidifies in very hard crystals. Unless it has been heated to bright redness, it combines with H_2O , with elevation of temperature. It is almost insoluble in acids and alkalies. H_2SO_4 , diluted with an equal bulk of H_2O , dissolves it slowly as $(\text{Al}_2)(\text{SO}_4)_3$. Fused potash and soda combine with it to form aluminates. It is not reduced by charcoal.

Aluminium Hydroxid—*Aluminium hydrate*—**Aluminii hydras** (U. S.)— $\text{Al}_2\text{H}_6\text{O}_6$ —156.2—is formed when a solution of aluminium salt is decomposed by an alkali, or alkaline carbonate. It constitutes a gelatinous mass, which, when dried, leaves an amorphous, translucent mass; and, when pulverized, a white, tasteless, amorphous powder. When the liquid in which it is formed contains coloring matters, these are carried down with it, and the dried deposits are used as pigments, called *lakes*.

When freshly precipitated, it is insoluble in H_2O ; soluble in acids, and in solutions of the fixed alkalies. When dried at a temperature above 50° (122° F.), or after 24 hours' contact with the mother liquor, its solubility is greatly diminished. With acids it

forms salts of aluminium; and with alkalis, aluminates of the alkaline metal. Heated to near redness, it is decomposed into Al_2O_3 , and H_2O . A soluble modification is obtained by dialyzing a solution of $\text{Al}_2\text{H}_6\text{O}_6$ in Al_2Cl_6 , or by heating a dilute solution of aluminium acetate for 24 hours.

Aluminates are for the most part crystalline, soluble compounds, obtained by the action of metallic oxides or hydroxids upon alumina. **Potassium aluminate**, $\text{K}_2\text{Al}_2\text{O}_4 + 3\text{Aq}$, is formed by dissolving recently precipitated aluminium hydroxid in potash solution. It forms white crystals, very soluble in H_2O , insoluble in alcohol; caustic and alkaline. By a large quantity of H_2O it is decomposed into aluminium hydroxid and a more alkaline salt, $\text{K}_6\text{Al}_4\text{O}_9$.

Sodium Aluminate.—The aluminate $\text{Na}_6\text{Al}_2\text{O}_6$ is formed when cryolite is heated with calcium carbonate (see sodium carbonate). Another salt, having the composition $\text{Na}_6\text{Al}_4\text{O}_9$, is prepared by heating to redness a mixture of 1 pt. sodium carbonate and 2 pts. of a native ferruginous aluminium hydrate (beauxite). Both salts are soluble in H_2O , and are decomposed by carbonic acid, with precipitation of aluminium hydroxid.

Aluminium Chlorid— Al_2Cl_6 —266.9—is prepared by passing Cl over a mixture of Al_2O_3 and C , heated to redness, or by heating clay in a mixture of gaseous HCl and vapor of CS_2 .

It crystallizes in colorless, hexagonal prisms; fusible; volatile; deliquescent; very soluble in H_2O and in alcohol. From a hot, concentrated solution, it separates in prisms with 12Aq. At very high temperatures Al_2Cl_6 appears to be dissociated into 2AlCl_3 .

The disinfectant called **chloralum** is a solution of impure Al_2Cl_6 .

Aluminium Sulfate—**Aluminii sulfas** (U. S.)— $(\text{Al}_2)(\text{SO}_4)_3 + 18\text{Aq}$ —342.2+324—is obtained by dissolving $\text{Al}_2\text{H}_6\text{O}_6$ in H_2SO_4 ; or (industrially) by heating clay with H_2SO_4 .

It crystallizes, with difficulty, in thin, flexible plates; soluble in H_2O ; very sparingly soluble in alcohol. Heated, it fuses in its Aq, which it gradually loses up to 200° (392° F.), when a white, amorphous powder, $(\text{Al}_2)(\text{SO}_4)_3$, remains: this is decomposed at a red heat, leaving a residue of pure alumina.

Alums—are double sulfates of the alkaline metals, and the higher sulfates of this, or the iron group. When crystallized, they have the general formula: $(\text{M}_2)^{\text{vi}}(\text{SO}_4)_3, \text{R}'_2\text{SO}_4 + 24\text{Aq}$, in which (M) may be (Fe_2) , (Mn_2) , (Cr_2) , (Al_2) , or (Ga_2) ; and R_2 may be K_2 , Na_2 , Rb_2 , Cs_2 , Tl_2 , or $(\text{NH}_4)_2$. They are isomorphous with each other.

Alumen (U. S.)— $\text{Al}_2(\text{SO}_4)_3, \text{K}_2\text{SO}_4 + 24\text{Aq}$ —516.5+432—is manufactured from "alum shale," and is formed when solutions of the sulfates of Al and K are mixed in suitable proportion.

It crystallizes in large, transparent, regular octahedra; has a sweetish, astringent taste, and is readily soluble in H_2O . Heated, it fuses in its Aq at 92° (197.6°F.); and gradually loses 45.5 per cent. of its weight of H_2O , as the temperature rises to near redness. The product, known as **burnt alum**=**alumen exsiccatum** (U. S.), is $(\text{Al})_2(\text{SO}_4)_3$, K_2SO_4 , and is slowly, but completely, soluble in 20–30 pts. H_2O . At a bright red heat, SO_2 and O are given off, and Al_2O_3 and potassium sulfate remain; at a higher temperature, potassium aluminate is formed. Its solutions are acid in reaction; dissolve Zn and Fe with evolution of H ; and deposit $\text{Al}_2\text{H}_6\text{O}_6$ when treated with ammonium hydroxid.

Alumen (Br.)— $\text{Al}_2(\text{SO}_4)_3$, $(\text{NH}_4)_2\text{SO}_4 + 24\text{Aq}$ —474.2+432—is the compound now usually met with as **alum**, both in this country and in England. It differs from potash alum in being more soluble in H_2O , between 20° – 30° (68° – 86°F.), and less soluble at other temperatures; and in the action of heat upon it. At 92° (197.6°F.) it fuses in its Aq; at 205° (401°F.), it loses its ammonium sulfate, leaving a white, hygroscopic substance, very slowly and incompletely soluble in H_2O . More strongly heated, it leaves alumina. Alum is used in dyeing, and in purification of water by precipitation.

Silicates—are very abundant in the different varieties of *clay*, *feldspar*, *albite*, *labradorite*, *mica*, etc. The clays are hydrated aluminium silicates, more or less contaminated with alkaline and earthy salts and iron, to which last certain clays owe their color. The purest is **kaolin**, or porcelain clay, a white or grayish powder. They are largely used in the manufacture of the different varieties of bricks, terra cotta, pottery, and porcelain. *Porcelain* is made from the purer clays, mixed with sand and feldspar; the former to prevent shrinkage, the latter to bring the mixture into partial fusion, and to render the product translucent. The fashioned articles are subjected to a first baking. The porous, baked clay is then coated with a *glaze*, usually composed of oxid of lead, sand and salt. During a second baking the glaze fuses, and coats the article with a hard, impermeable layer. The coarser articles of pottery are glazed by throwing sodium chlorid into the fire; the salt is volatilized, and on contact with the hot aluminium silicate, deposits a coating of the fusible sodium silicate, which hardens on cooling.

Analytical Characters.—(1) Potash, or soda: white ppt., soluble in excess. (2) Ammonium hydroxid: white ppt., almost insoluble in excess, especially in presence of ammoniacal salts. (3) Sodium phosphate: white ppt., readily soluble in KHO and NaHO , but not in NH_4HO ; soluble in mineral acids, but not in acetic acid. (4) Blow-pipe—on charcoal does not fuse, and moistened with cobalt nitrate solution turns dark sky-blue.

VI. NICKEL GROUP.

NICKEL—COBALT.

These two elements bear some resemblance chemically to those of the Fe group; from which they differ in forming, so far as known, no compounds similar to the ferrates, chromates, and manganates, unless the barium cobaltite, described by Rousseau, be such. They form compounds corresponding to Fe_2O_3 , but those corresponding to the ferric salts are either wanting or exceedingly unstable.

NICKEL.

Symbol=Ni—*Atomic weight*=58 (O=16:58.7; H=1:58.22)—*Sp. gr.*=8.637.

Occurs in combination with S, and with S and As.

It is a white metal, hard, slightly magnetic, not tarnished in air. *German silver* is an alloy of Ni, Cu, and Zn. Nickel is now extensively used for plating upon other metals, and for the manufacture of dishes, etc., for use in the laboratory. Its salts are green.

Nickelous Sulfate— NiSO_4 —is obtained by dissolving the metal, hydroxid or carbonate in H_2SO_4 . It forms green crystals with 7 Aq. and combines with $(\text{NH}_4)_2\text{SO}_4$ to form a double sulfate, used in the nickel-plating bath, for which use it must be free from K or Na.

Analytical Characters.—(1) Ammonium sulfhydrate: black ppt.; insoluble in excess. (2) Potash or soda: apple-green ppt., in absence of tartaric acid; insoluble in excess. (3) Ammonium hydroxid: apple-green ppt.; soluble in excess; forming a violet solution, which deposits the apple-green hydrate, when heated with KHO.

COBALT.

Symbol=Co—*Atomic weight*=59 (O=16:59; H=59.53)—*Sp. gr.*=8.5-8.7.

Occurs in combination with As and S. Its salts are red when hydrated, and usually blue when anhydrous. Its phosphate is used as a blue pigment.

Analytical Characters.—(1) Ammonium sulfhydrate: black ppt.; insoluble in excess. (2) Potash: blue ppt.; turns red, slowly in the cold, quickly when heated; not formed in the cold in the presence of NH_4 salts. (3) Ammonium hydroxid: blue ppt.; turns red in absence of air, green in its presence.

VII. COPPER GROUP.

COPPER—MERCURY.

Each of these elements forms two series of compounds. One contains compounds of the bivalent group $\left(\begin{smallmatrix} \text{Cu} \\ | \\ \text{Cu} \end{smallmatrix}\right)''$ or $(\text{Hg}_2)''$, which are designated by the termination *ous*; the other contains compounds of single, bivalent atoms Cu'' or Hg'' , which are designated by the termination *ic*.

COPPER.

Symbol=Cu (*Cuprum*)—*Atomic weight*=63 (O=16:63.6; H=1:63.09)—*Molecular weight*=127 (?)—*Sp. gr.*=8.914–8.952—*Fuses at* 1091° (1996° F.).

Occurrence.—It is found free, in crystals or amorphous masses, sometimes of great size; also as sulfid, *copper pyrites*; oxid, *ruby ore* and *black oxid*; and basic carbonate, *malachite*.

Properties.—*Physical*.—A yellowish-red metal; dark-brown when finely divided; very malleable, ductile, and tenacious; a good conductor of heat and electricity; has a peculiar, metallic taste, and a characteristic odor.

Chemical.—It is unaltered in dry air at the ordinary temperature; but, when heated to redness, is oxidized to CuO . In damp air it becomes coated with a brownish film of oxid; a green film of basic carbonate; or, in salt air, a green film of basic chlorid. Hot H_2SO_4 dissolves it with formation of CuSO_4 and SO_2 . It is dissolved by HNO_3 with formation of $\text{Cu}(\text{NO}_3)_2$ and NO ; and by HCl with liberation of H_2 . Weak acids form with it soluble salts, in presence of air and moisture. It is dissolved by NH_4HO , in presence of air, with formation of a blue solution. It combines directly with Cl , frequently with light.

Oxids.—*Cuprous Oxid*—*Suboxid or red oxid of copper*— $(\text{Cu}_2)\text{O}$ —143.2—is formed by calcining a mixture of $(\text{Cu}_2)\text{Cl}_2$ and Na_2CO_3 ; or a mixture of CuO and Cu . It is a red or yellow powder; permanent in air; sp. gr. 5.749–6.093; fuses at a red heat; easily reduced by C or H . Heated in air it is converted into CuO .

Cupric Oxid—*Binoxid or black oxid of copper*— CuO —79.6—is prepared by heating Cu to dull redness in air; or by calcining $\text{Cu}(\text{NO}_3)_2$; or by prolonged boiling of the liquid over a precipitate, produced by heating a solution of a cupric salt, in presence of glucose, with KHO . By the last method it is sometimes produced in Trommer's test for glucose, when an excessive quantity of CuSO_4 has been used.

It is a black, or dark reddish-brown, amorphous solid; readily reduced by C, H, Na, or K at comparatively low temperatures. When heated with organic substances, it gives up its O, converting the C into CO₂, and the H into H₂O: $C_2H_6O + 6CuO = 6Cu + 2CO_2 + 3H_2O$; a property which renders it valuable in organic analysis, as by heating a known weight of organic substance with CuO, and weighing the amount of CO₂ and H₂O produced, the percentage of C and H may be obtained. It dissolves in acids with formation of salts.

Hydroxids.—**Cuprous Hydroxid**— $(Cu)_2H_2O_2(?)$ —160.4 (?)—is formed as a yellow or red powder when mixed solutions of CuSO₄ and KHO are heated in presence of glucose. By boiling the solution it is rapidly dehydrated with formation of $(Cu_2)O$.

Cupric Hydroxid— CuH_2O_2 —97.6—is formed by the action of KHO upon solution of CuSO₄, in absence of reducing agents and in the cold. It is a bluish, amorphous powder; very unstable, and readily dehydrated, with formation of CuO.

Sulfids.—**Cuprous Sulfid**—*Subsulfid or protosulfid of copper*— Cu_2S —159.2—occurs in nature as *copper glance* or *chalcosine*, and in many double sulfids, *pyrites*.

Cupric Sulfid— CuS —95.6—is formed by the action of H₂S, or of NH₄HS, on solutions of cupric salts. It is almost black when moist, greenish-brown when dry. Hot HNO₃ oxidizes it to CuSO₄; hot HCl converts it into CuCl₂, with separation of S, and formation of H₂S. It is sparingly soluble in NH₄HS, its solubility being increased by the presence of organic matter.

Chlorids.—**Cuprous Chlorid**—*Subchlorid or protochlorid*— $(Cu_2)Cl_2$ —198.1—is prepared by heating Cu with one of the chlorids of Hg; by dissolving $(Cu_2)O$ in HCl, without contact of air; or by the action of reducing agents on solutions of CuCl₂. It is a heavy, white powder; turns violet and blue by exposure to light; soluble in HCl; insoluble in H₂O. It forms a crystallizable compound with CO; and its solution in HCl is used in analysis to absorb that gas.

Cupric Chlorid—*Chlorid or deutochlorid*— $CuCl_2$ —134.5—is formed by dissolving Cu in aqua regia. If the Cu be in excess, it reduces CuCl₂ to $(Cu_2)Cl_2$. It crystallizes in bluish-green, rhombic prisms with 2 Aq; deliquescent; very soluble in H₂O and in alcohol.

Cupric Nitrate— $Cu(NO_3)_2$ —187.6—is formed by dissolving Cu, CuO, or CuCO₃ in HNO₃. It crystallizes at 20°–25° (68°–77° F.) with 3 Aq; below 20° (68° F.) with 6 Aq, forming blue, deliquescent needles. Strongly heated, it is converted into CuO.

Cupric Sulfate—*Blue vitriol*—*Blue stone*—**Cupri sulfas** (U. S.; Br.)— $CuSO_4 + 5Aq$ —159.6+90—is prepared: (1) by roasting CuS; (2) from the water of copper mines; (3) by exposing Cu, moistened with dilute H₂SO₄, to air; (4) by heating Cu with H₂SO₄.

As ordinarily crystallized, it is in fine, blue, oblique prisms; soluble in H_2O ; insoluble in alcohol; efflorescent in dry air at 15° (59° F.), losing 2 Aq. At 100° (212° F.) it still retains 1 Aq, which it loses at 230° (446° F.), leaving a white, amorphous powder of the anhydrous salt, which, on taking up H_2O , resumes its blue color. Its solutions are blue, acid, styptic, and metallic in taste.

When NH_4HO is added to a solution of CuSO_4 , a bluish-white precipitate falls, which redissolves in excess of the alkali, to form a deep blue solution. Strong alcohol floated over the surface of this solution separates long, right rhombic prisms, having the composition $\text{CuSO}_4 \cdot 4\text{NH}_3 + \text{H}_2\text{O}$, which are very soluble in H_2O . This solution constitutes **ammonio-sulfate of copper** or **aqua sapphirina**.

Cupric Arsenite—Scheele's green—Mineral green—is a mixture of cupric arsenite, HCuAsO_3 , and hydroxid; prepared by adding potassium arsenite to solution of CuSO_4 . It is a grass-green powder, insoluble in H_2O ; soluble in NH_4HO , or in acids. Exceedingly poisonous.

Schweinfurt Green—Mitis green or Paris green—is the most frequently used, and the most dangerous of the cupro-arsenical pigments. It is prepared by adding a thin paste of neutral cupric acetate with H_2O to a boiling solution of arsenous acid, and continuing the boiling during a further addition of acetic acid. It is an insoluble, green, crystalline powder, having the composition $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu} + 3\text{Cu}(\text{AsO}_2)_2$, and is therefore cupric aceto-metarsenite. It is decomposed by prolonged boiling in H_2O , by aqueous solutions of the alkalis, and by the mineral acids.

Carbonates.—The existence of cuprous carbonate is doubtful. **Cupric carbonate**— CuCO_3 —exists in nature, but has not been obtained artificially. **Dicupric carbonate**— $\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2$ —exists in nature as **malachite**. When a solution of a cupric salt is decomposed by an alkaline carbonate, a bluish precipitate, having the composition $\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2 + \text{H}_2\text{O}$, is formed, which, on drying, loses H_2O , and becomes green; it is used as a pigment under the name **mineral green**. **Tricupric carbonate—Sesquicarbonate of copper**— $2(\text{CuCO}_3) \cdot \text{CuH}_2\text{O}_2$ —exists in nature as a blue mineral, called **azurite** or **mountain blue**, and is prepared by a secret process for use as a pigment known as **blue ash**.

Acetates.—**Cupric Acetate—Diacetate—Crystals of Venus—Cupri acetat** (U. S.)— $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{Aq} - 181.6 + 18$ —is formed when CuO or **verdigris** is dissolved in acetic acid; or by decomposition of a solution of CuSO_4 by $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. It crystallizes in large, bluish-green prisms, which lose their Aq at 140° (284° F.). At 240° – 260° (464° – 500° F.) they are decomposed with liberation of glacial acetic acid.

Basic Acetates.—**Verdigris**—is a substance prepared by exposing to air piles composed of alternate layers of grape-skins and plates of copper, and removing the bluish-green coating from the copper. It is a mixture, in varying proportions, of three different substances: $(C_2H_3O_2)_2Cu_2H_2O_2 + 5Aq$; $[(C_2H_3O_2)_2Cu]_2, CuH_2O_2 + 5Aq$; and $(C_2H_3O_2)_2Cu, 2(CuH_2O_2)$.

Analytical Characters.—**CUPROUS**—are very unstable and readily converted into cupric compounds. (1) Potash: white ppt.; turning brownish. (2) Ammonium hydroxid, in absence of air: a colorless liquid; turns blue in air.

CUPRIC—are white when anhydrous; when soluble in H_2O they form blue or green, acid solutions. (1) Hydrogen sulfid: black ppt.; insoluble in KHS or NaHS; sparingly soluble in NH_4HS ; soluble in hot concentrated HNO_3 and in KCN. (2) Alkaline sulphydrates: same as H_2S . (3) Potash or soda: pale blue ppt.; insoluble in excess. If the solution be heated over the ppt., the latter contracts and turns black. (4) Ammonium hydroxid, in small quantity: pale blue ppt.; in larger quantity: deep blue solution. (5) Potassium or sodium carbonate: greenish-blue ppt.; insoluble in excess; turning black when the liquid is boiled. (6) Ammonium carbonate: pale blue ppt.; soluble with deep-blue color in excess. (7) Potassium cyanid: greenish-yellow ppt.; soluble in excess. (8) Potassium ferrocyanid: chestnut-brown ppt.; insoluble in weak acids; decolorized by KHO. (9) Iron is coated with metallic Cu.

Action on the Economy.—The opinion, formerly universal among toxicologists, that all the compounds of copper are poisonous, has been much modified by later researches. Certain of the copper compounds, such as the sulfate, having a tendency to combine with protein and other animal substances, produce symptoms of irritation by their direct local action, when brought in contact with the gastr'ic or intestinal mucous membrane. One of the characteristic symptoms of such irritation is the vomiting of a greenish matter, which develops a blue color upon the addition of NH_4HO .

Cases are not wanting in which severe illness, and even death, has followed the use of food which has been in contact with imperfectly tinned copper vessels. Cases in which nervous and other symptoms referable to a truly poisonous action have occurred. As, however, it has also been shown that non-irritant, *pure* copper compounds may be taken in considerable doses with impunity, it appears at least probable that the poisonous action attributed to copper is due to other substances. The tin and solder used in the manufacture of copper utensils contain lead, and in some cases of so-called copper-poisoning, the symptoms have been such as are as consistent with lead-poisoning as with copper-poisoning. Copper is also notoriously

liable to contamination with arsenic, and it is by no means improbable that compounds of that element are the active poisonous agents in some cases of supposed copper-intoxication. Nor is it improbable that articles of food allowed to remain exposed to air in copper vessels should undergo those peculiar changes which result in the formation of poisonous substances, such as the sausage- or cheese-poisons, or the ptomaines.

The treatment, when irritant copper compounds have been taken, should consist in the administration of white of egg or of milk, with whose proteins an inert compound is formed by the copper salt. If vomiting do not occur spontaneously, it should be induced by the usual methods.

The detection of copper in the viscera after death is not without interest, especially if arsenic have been found, in which case its discovery or non-discovery enables us to differentiate between poisoning by the arsenical greens, and that by other arsenical compounds. The detection of mere traces of copper is of no significance, because, although copper is not a physiological constituent of the body, it is almost invariably present, having been taken with the food.

Pickles and canned vegetables are sometimes intentionally *greened* by the addition of copper; this fraud is readily detected by inserting a large needle into the pickle or other vegetable; if copper be present the steel will be found to be coated with copper after half an hour's contact.

MERCURY.

Symbol=Hg (*Hydrargyrum*)—*Atomic weight*=200 (O=16:200.3; H=1:198.7)—*Molecular weight*=198.7—*Sp. gr. of liquid*=13.596; *of vapor*=6.97—*Fuses at* -38.8° (-37.9° F.)—*Boils at* 358° (676.4° F.).

Occurrence.—Chiefly as *cinnabar* (HgS); also in small quantity free and as chlorid.

Preparation.—The commercial product is usually obtained by simple distillation in a current of air: $\text{HgS} + \text{O}_2 = \text{Hg} + \text{SO}_2$. If required pure, it must be freed from other metals by distillation, and agitation of the redistilled product with mercurous nitrate solution, solution of Fe_2Cl_6 , or dilute HNO_3 .

Properties.—*Physical.*—A bright metallic liquid; volatile at all temperatures. Crystallizes in octahedra of sp. gr. 14.0. When pure, it rolls over a smooth surface in round drops. The formation of tear-shaped drops indicates the presence of impurities.

Chemical.—If pure, it is not altered by air at the ordinary temperature, but, if contaminated with foreign metals, its surface becomes dimmed. Heated in air, it is oxidized superficially to HgO . It

does not decompose H_2O . It combines directly with Cl, Br, I, and S. It alloys readily with most metals to form **amalgams**. It amalgamates with Fe and Pt only with difficulty. Hot, concentrated, H_2SO_4 dissolves it, with evolution of SO_2 , and formation of $HgSO_4$. It dissolves in cold HNO_3 , with formation of a nitrate.

Elementary mercury is insoluble in H_2O , and probably in the digestive liquids. It enters, however, into the formation of three medicinal agents: **hydrargyrum cum creta** (U. S.; Br.); **massa hydrargyri** (U. S.)=**pilula hydrargyri** (Br.); and **unguentum hydrargyri** (U. S.; Br.), all of which owe their efficacy, not to the metal itself, but to a certain proportion of oxid, produced during their manufacture. The fact that blue mass is more active than mercury with chalk is due to the greater proportion of oxid contained in the former. It is also probable that absorption of vapor of Hg by cutaneous surfaces is attended by its conversion into $HgCl_2$.

Oxids.—**Mercurous Oxid**—*Protoxid or black oxid of mercury*—(Hg_2)O—416.6—is obtained by adding a solution of $(Hg_2)(NO_3)_2$ to an excess of solution of KHO. It is a brownish black, tasteless powder; very prone to decomposition into HgO and Hg. It is converted into $(Hg_2)Cl_2$ by HCl; and by other acids into the corresponding mercurous salts.

It is formed by the action of CaH_2O_2 on mercurous compounds, and exists in **black wash**.

Mercuric Oxid—*Red, or binoxid of mercury*—**Hydrargyri oxidum flavum** (U. S.; Br.)—**Hydrargyri oxidum rubrum** (U. S.; Br.)—HgO—216.3—is prepared by two methods: (1) by calcining $Hg(NO_3)_2$, as long as brown fumes are given off (*Hydr. oxid. rubr.*); or, (2) by precipitating a solution of a mercuric salt by excess of KHO (*Hydr. oxid. flavum*). The products obtained, although the same in composition, differ in physical characters and in the activity of their chemical actions. That obtained by (1) is red and crystalline; that obtained by (2) is yellow and amorphous. The latter is much the more active in its chemical and medicinal actions.

It is very sparingly soluble in H_2O , the solution having an alkaline reaction, and a metallic taste. It exists both in solution and in suspension in **yellow wash**, prepared by the action of CaH_2O_2 on a mercuric compound.

Exposed to light and air, it turns black, more rapidly in presence of organic matter, giving off O, and liberating Hg : $HgO = Hg + O$. It decomposes the chlorids of many metallic elements in solution, with formation of a metallic oxid and mercuric oxychlorids. It combines with alkaline chlorids to form soluble double chlorids, called **chloromercurates** or **chlorhydrargyrates**; and forms similar compounds with alkaline iodids and bromids.

Sulfids.—**Mercurous Sulfid**— $(\text{Hg}_2)\text{S}$ —432.6—a very unstable compound, formed by the action of H_2S on mercurous salts.

Mercuric Sulfid—*Red sulfid of mercury*—**Cinnabar**—**Vermilion**—**Hydrargyri sulfidum rubrum** (U. S.)— HgS —232.3—exists in nature in amorphous red masses, or in red crystals, and is the chief ore of Hg. If Hg and S be ground up together in the cold, or if a solution of a mercuric salt be completely decomposed by H_2S , a black sulfid is obtained, which is the *Æthiops mineralis* of the older pharmacists.

A red sulfid is obtained for use as a pigment (*vermilion*), by agitating for some hours at 60° (140° F.) a mixture of Hg, S, KHO, and H_2O . It is a fine, red powder, which turns brown, and finally black, when heated. Heated in air, it burns to SO_2 and Hg. It is decomposed by strong H_2SO_4 , but not by HNO_3 or HCl.

Chlorids.—**Mercurous Chlorid**—*Protochlorid or mild chlorid of mercury*—**Calomel**—**Hydrargyri chloridum mite** (U. S.)—**Hydrargyri subchloridum** (Br.)— $(\text{Hg}_2)\text{Cl}_2$ —471.5—is now principally obtained by mutual decomposition of NaCl and $(\text{Hg}_2)\text{SO}_4$. Mercuric sulfate is first obtained by heating together 2 pts. Hg and 3 pts. H_2SO_4 ; the product is then caused to combine with a quantity of Hg equal to that first used, to form $(\text{Hg}_2)\text{SO}_4$; which is then mixed with dry NaCl, and the mixture heated in glass vessels, connected with condensing chambers; $2\text{NaCl} + (\text{Hg}_2)\text{SO}_4 = \text{Na}_2\text{SO}_4 + (\text{Hg}_2)\text{Cl}_2$.

In practice, varying quantities of HgCl_2 are also formed, and must be removed from the product by washing with boiled, distilled H_2O , until the washings no longer precipitate with NH_4HO . The presence of HgCl_2 in calomel may be detected by the formation of a black stain upon a bright copper surface, immersed in the calomel, moistened with alcohol; or by the production of a black color by H_2S in H_2O which has been in contact with and filtered from calomel so contaminated.

Calomel is also formed in a number of other reactions: (1) By the action of Cl upon excess of Hg. (2) By the action of Hg upon Fe_2Cl_6 . (3) By the action of HCl, or of a chlorid, upon $(\text{Hg}_2)\text{O}$, or upon a mercurous salt. (2) By the action of reducing agents, including Hg, upon HgCl_2 .

Calomel crystallizes in nature, and, when sublimed, in quadratic prisms. When precipitated it is deposited as a heavy, amorphous, white powder, faintly yellowish, and producing a yellowish mark when rubbed upon a dark surface. It sublimes, without fusing, between 420° and 500° (788° – 932° F.), is insoluble in cold H_2O and in alcohol; soluble in boiling H_2O to the extent of 1 part in 12,000. When boiled with H_2O for some time, it suffers partial decomposition, Hg is deposited and HgCl_2 dissolves.

Although Hg_2Cl_2 is insoluble in H_2O , in dilute HCl and in pepsin solution, it is dissolved at the body temperature in an aqueous solution of pepsin acidulated with HCl .

When exposed to light, calomel becomes yellow, then gray, owing to partial decomposition, with liberation of Hg and formation of HgCl_2 : $(\text{Hg}_2)\text{Cl}_2 = \text{Hg} + \text{HgCl}_2$. It is converted into HgCl_2 by Cl or aqua regia: $(\text{Hg}_2)\text{Cl}_2 + \text{Cl}_2 = 2\text{HgCl}_2$. In the presence of H_2O , I converts it into a mixture of HgCl_2 and HgI_2 : $(\text{Hg}_2)\text{Cl}_2 + \text{I}_2 = \text{HgCl}_2 + \text{HgI}_2$. It is also converted into HgCl_2 by HCl and by alkaline chlorids: $(\text{Hg}_2)\text{Cl}_2 = \text{HgCl}_2 + \text{Hg}$. This change occurs in the stomach when calomel is taken internally, and that to such an extent when large quantities of NaCl are taken with the food, that calomel cannot be used in naval practice as it may be with patients who do not subsist upon salt provisions. It is converted by KI into $(\text{Hg}_2)\text{I}_2$: $(\text{Hg}_2)\text{Cl}_2 + 2\text{KI} = 2\text{KCl} + (\text{Hg}_2)\text{I}_2$; which is then decomposed by excess of KI into Hg and HgI_2 , the latter dissolving: $(\text{Hg}_2)\text{I}_2 = \text{Hg} + \text{HgI}_2$. Solutions of the sulfates of Na , K and NH_4 dissolve notable quantities of $(\text{Hg}_2)\text{Cl}_2$. The hydroxids and carbonates of K and Na decompose it with formation of $(\text{Hg}_2)\text{O}$: $(\text{Hg}_2)\text{Cl}_2 + \text{Na}_2\text{CO}_3 = (\text{Hg}_2)\text{O} + \text{CO}_2 + 2\text{NaCl}$; and the $(\text{Hg}_2)\text{O}$ so formed is decomposed into HgO and Hg . If alkaline chlorids be also present, they react upon the HgO so produced, with formation of HgCl_2 .

Mercuric Chlorid—*Perchlorid or bichlorid of mercury*—**Corrosive sublimate**—*Hydrargyri chloridum corrosivum* (U. S.); *Hydrargyri perchloridum* (Br.)— HgCl_2 —271.2—is prepared by heating a mixture of 5 pts. dry HgSO_4 with 5 pts. dry NaCl , and 1 pt. MnO_2 in a glass vessel communicating with a condensing chamber.

It crystallizes by sublimation in octahedra, and by evaporation of its solutions in flattened, right rhombic prisms; fuses at 265° (509° F.), and boils at about 295° (563° F.); soluble in H_2O and in alcohol; very soluble in hot HCl , the solution gelatinizing on cooling. Its solutions have a disagreeable, acid, styptic taste, and are highly poisonous. Although HgCl_2 is heavier than water (sp. gr.=5.4) when the crystalline powder is thrown upon water a portion floats for some time.

It is easily reduced to $(\text{Hg}_2)\text{Cl}_2$ and Hg , and its aqueous solutions are so decomposed when exposed to light; a change which is retarded by the presence of NaCl . Heated with Hg , it is converted into $(\text{Hg}_2)\text{Cl}_2$. When dry HgCl_2 , or its solution, is heated with Zn , Cd , Ni , Fe , Pb , Cu , or Bi , those elements remove part or all of its Cl , with separation of $(\text{Hg}_2)\text{Cl}_2$ or Hg . Its solution is decomposed by H_2S , with separation of a yellow sulfochlorid, which, with an excess of the gas, is converted into black HgS . It is soluble without decomposition in H_2SO_4 , HNO_3 , and HCl . It is decomposed by KHO or

NaHO, with separation of a brown oxychlorid if the alkaline hydroxid be in limited quantity; or of the orange-colored HgO if it be in excess. A similar decomposition is effected by CaH_2O_2 and MgH_2O_2 ; which does not, however, take place in presence of an alkaline chlorid, or of certain organic matters, such as sugar and gum. Many organic substances decompose it into $(\text{Hg}_2)\text{Cl}_2$ or Hg, especially under the influence of sunlight. Thus in sunlight it is reduced by oxalic acid, which is itself oxidized to carbon dioxide: $2\text{HgCl}_2 + \text{C}_2\text{O}_4\text{H}_2 = \text{Hg}_2\text{Cl}_2 + 2\text{CO}_2 + 2\text{HCl}$. For this reason it behaves as an oxidant: $2\text{HgCl}_2 + \text{H}_2\text{O} = \text{Hg}_2\text{Cl}_2 + 2\text{HCl} + \text{O}$. Albumen forms with it a white precipitate, which is insoluble in H_2O , but soluble in an excess of fluid albumen and in solutions of alkaline chlorids. It readily combines with metallic chlorids, to form soluble double chlorids, called **chloromercurates** or **chlorhydrargyrates**. One of these, obtained in flattened, rhombic prisms, by the cooling of a boiling solution of HgCl_2 and NH_4Cl , has the composition $\text{Hg}(\text{NH}_4)_2\text{Cl}_2 + \text{Aq}$, and was formerly known as *sal alembroth* or *sal sapientie*. It is a very energetic germicide.

Mercurammonium Chlorid—*Mercury chloramidid*—*Infusible white precipitate*—*Ammoniated mercury*—**Hydrargyrum ammoniatum** (U. S.; Br.)— NH_2HgCl —251.8—is prepared by adding a slight excess of NH_4HO to a solution of HgCl_2 . It is a white powder, insoluble in alcohol, ether, and cold H_2O : decomposed by hot H_2O , with separation of a heavy, yellow powder. It is entirely volatile, without fusion. The *fusible white precipitate* is formed in small crystals when a solution containing equal parts of HgCl_2 and NH_4Cl is decomposed by Na_2CO_3 . It is **mercurdiammonium chlorid**, $\text{NH}_2\text{Hg}, \text{NH}_4\text{Cl}_2$.

Iodids.—**Mercurous Iodid**—*Protoiodid* or *yellow iodid*—**Hydrargyri iodidum viride** (U. S.; Br.)— Hg_2I_2 —654.3—is prepared by grinding together 200 pts. Hg and 127 pts. I with a little alcohol, until a green paste is formed. It is a greenish-yellow, amorphous powder, insoluble in H_2O and in alcohol. When heated, it turns brown, and volatilizes completely. When exposed to light, or even after a time in the dark, it is decomposed into HgI_2 and Hg. The same decomposition is brought about instantly by KI; more slowly by solutions of alkaline chlorids, and by HCl when heated. NH_4HO dissolves it with separation of a gray precipitate.

Mercuric Iodid—*Binioidid* or *red iodid*—**Hydrargyri iodidum rubrum** (U. S.; Br.)— HgI_2 —454—is obtained by double decomposition between HgCl_2 and KI, care being had to avoid too great an excess of the alkaline iodid, that the soluble potassium iodhydrargyrate may not be formed.

It is sparingly soluble in H_2O ; but forms colorless solutions with alcohol. It dissolves readily in many dilute acids, and in solutions of

ammoniacal salts, alkaline chlorids, and mercuric salts; and in solutions of alkaline iodids. Iron and copper convert it into $(\text{Hg}_2)\text{I}_2$, then into Hg. The hydroxids of K and Na decompose it into oxid or oxyiodid, and combine with another portion to form iodhydrargyrites, which dissolve. NH_4HO separates from its solution a brown powder, and forms a yellow solution, which deposits white flocks.

Mercuric Cyanid—*Hydrargyri cyanidum* (U. S.)— $\text{Hg}(\text{CN})_2$ —252.3—is best prepared by heating together, for a quarter of an hour, potassium ferrocyanid, 1 pt.; HgSO_4 , 2 pts.; and H_2O , 8 pts. It crystallizes in quadrangular prisms; soluble in 8 pts. of H_2O , much less soluble in alcohol; highly poisonous. When heated dry it blackens, and is decomposed into $(\text{CN})_2$ and Hg; if heated in presence of H_2O it yields HCN, Hg, CO_2 , and NH_3 . Hot concentrated H_2SO_4 , and HCl, HBr, HI, and H_2S in the cold decompose it, with liberation of HCN. It is not decomposed by alkalis.

Nitrates.—There exist, besides the normal nitrates: $(\text{Hg}_2)(\text{NO}_3)_2$, and $\text{Hg}(\text{NO}_3)_2$, three basic mercurous nitrates, three basic mercuric nitrates, and a mercurioso-mercuric nitrate.

Mercurous Nitrate— $(\text{Hg}_2)(\text{NO}_3)_2 + 2\text{Aq}$ —524.6+36—is formed when excess of Hg is digested with HNO_3 , diluted with $\frac{1}{2}$ vol. H_2O ; until short, prismatic crystals separate.

It effloresces in air; fuses at 70° (158°F.); dissolves in a small quantity of hot H_2O , but with a larger quantity is decomposed with separation of the yellow, basic **trimercuric nitrate**, $\text{Hg}(\text{NO}_3)_2, 2\text{HgO} + \text{Aq}$.

Dimercurous Nitrate— $(\text{Hg}_2)(\text{NO}_3)_2, \text{Hg}_2\text{O} + \text{Aq}$ —941.2+18—is formed by acting upon the preceding salt with cold H_2O until it turns lemon-yellow; or by extracting with cold H_2O the residue of evaporation of the product obtained by acting upon excess of Hg with concentrated HNO_3 .

Trimmercurous Nitrate— $(\text{Hg}_2)_2(\text{NO}_3)_4, \text{Hg}_2\text{O} + 3\text{Aq}$ —1465.8+54—is obtained in large, rhombic prisms, when excess of Hg is boiled with HNO_3 , diluted with 5 pts. H_2O , for 5–6 hours, the loss by evaporation being made up from time to time.

Mercuric Nitrate— $\text{Hg}(\text{NO}_3)_2$ —324.3—is formed when Hg or HgO is dissolved in excess of HNO_3 , and the solution evaporated at a gentle heat. A syrupy liquid is obtained, which, over quicklime, deposits large, deliquescent crystals, having the composition $2[\text{Hg}(\text{NO}_3)_2] + \text{Aq}$, while there remains an uncrystallizable liquid, $\text{Hg}(\text{NO}_3)_2 + 2\text{Aq}$.

This salt is soluble in H_2O , and exists in the **Liq. hydrargyri nitratis** (U. S.), **Liq. hydrargyri nitratis acidus** (Br.); in the volumetric standard solution used in *Liebig's process* for urea; and probably in *citrine ointment*—**Ung. hydrar. nitratis** (U. S.; Br.).

Dimercuric Nitrate— $\text{Hg}(\text{NO}_3)_2$, $\text{HgO} + \text{Aq}$ —540.6—is formed when HgO is dissolved to saturation in hot HNO_3 , diluted with 1 vol. H_2O ; and crystallizes on cooling. It is decomposed by H_2O into trimercuric nitrate, $\text{Hg}(\text{NO}_3)_2$, 2HgO , and $\text{Hg}(\text{NO}_3)_2$.

Hexamercuric Nitrate— $\text{Hg}(\text{NO}_3)_2$, 5HgO —1405.8—is formed as a red powder, by the action of H_2O on trimercuric nitrate.

Sulfates.—**Mercurous Sulfate**— $(\text{Hg}_2)\text{SO}_4$ —495.4—is a white, crystalline powder, formed by gently heating together 2 pts. Hg and 3 pts. H_2SO_4 , and causing the product to combine with 2 pts. Hg . Heated with NaCl it forms $(\text{Hg}_2)\text{Cl}_2$.

Mercuric Sulfate—**Hydrargyri sulfas** (Br.)— HgSO_4 —296.3—is obtained by heating together Hg and H_2SO_4 , or Hg , H_2SO_4 , and HNO_3 . It is a white, crystalline, anhydrous powder, which, on contact with H_2O , is decomposed with formation of trimercuric sulfate, HgSO_4 , 2HgO ; a yellow, insoluble powder, known as turpeth mineral=**Hydrargyri subsulfas flavus** (U. S.).

Analytical Characters.—**MERCUROUS.**—(1) Hydrochloric acid: white ppt.; insoluble in H_2O and in acids; turns black with NH_4HO ; when boiled with HCl , deposits Hg , while HgCl_2 dissolves. (2) Hydrogen sulfid: black ppt.; insoluble in alkaline sulfhydrates, in dilute acids, and in KCN ; partly soluble in boiling HNO_3 . (3) Potash: black ppt.; insoluble in excess. (4) Potassium iodid: greenish ppt.; converted by excess into Hg , which is deposited, and HgI_2 , which dissolves.

MERCURIC.—(1) Hydrogen sulfid: black ppt. If the reagent be slowly added, the ppt. is first white, then orange, finally black. (2) Ammonium sulfhydrate: black ppt.; insoluble in excess, except in the presence of organic matter. (3) Potash or soda: yellow ppt.; insoluble in excess. (4) Ammonium hydroxid: white ppt.; soluble in great excess and in solutions of NH_4 salts. (5) Potassium carbonate: red ppt. (6) Potassium iodid: yellow ppt., rapidly turning to salmon color, then to red; easily soluble in excess of KI , or in great excess of mercuric salt. (7) Stannous chlorid, in small quantity: white ppt.; in larger quantity: gray ppt.; and when boiled: deposit of globules of Hg .

Action on the Economy.—Mercury, in the metallic form, is without action upon the animal economy so long as it remains such. On contact, however, with alkaline chlorids it is converted into a soluble double chlorid, and this the more readily the greater the degree of subdivision of the metal. The mercurials insoluble in dilute HCl are also inert until they are converted into soluble compounds.

Mercuric chlorid, a substance into which many other compounds of Hg are converted when taken into the stomach or applied to the skin, not only has a distinctly corrosive action, by virtue of its ten-

dency to unite with protein bodies, but, when absorbed, it produces well-marked poisonous effects, somewhat similar to those of arsenical poisoning. Indeed, owing to its corrosive action, and to its greater solubility and more rapid absorption, it is a more dangerous poison than As_2O_3 . In poisoning by $HgCl_2$, the symptoms begin sooner after the ingestion of the poison than in arsenical poisoning, and those phenomena referable to the local action of the toxic are more intense. But the entire duration of the poisoning is greater. In fatal cases, death usually occurs in 5 to 12 days.

The treatment should consist in the administration of white of egg, not in too great quantity, and the removal of the compound formed, by emesis, before it has had time to redissolve in the alkaline chlorids contained in the stomach.

Absorbed Hg tends to remain in the system in combination with protein bodies, from which it may be set free, or, more properly, brought into soluble combination, at a period quite removed from the date of last administration, by the exhibition of alkaline iodids.

Mercury is eliminated principally by the saliva and urine, in which it may be readily detected. The fluid is faintly acidulated with HCl, and in it is immersed a short bar of Zn, around which a spiral of dentist's gold foil is wound in such a way as to expose alternate surfaces of Zn and Au. After 24 hours, if the saliva or urine contain Hg, the Au will be whitened by amalgamation; and, if dried and heated in the closed end of a small glass tube, will give off Hg, which condenses in globules, visible with the aid of a magnifier, in the cold part of the tube.

ORGANIC CHEMISTRY.

COMPOUNDS OF CARBON.

In the beginning of the nineteenth century chemistry was divided into the two sections of **inorganic** and **organic**. The former treated of the products of the mineral world, the latter of substances produced in *organized* bodies, vegetable or animal. This subdivision, originally made upon the supposition that organic substances could only be produced by "vital processes," is retained only for convenience and because of the great number of the carbon compounds.

When it was found that organic substances were made up of a very few elements, and that they all contained carbon, Gmelin proposed to consider as organic substances all such as contained more than one atom of C, his object in thus limiting the minimum number of C atoms being that substances containing one atom of C, such as carbon dioxid and marsh gas, are formed in the mineral kingdom, and consequently, according to then existing views, could not be considered as *organic*. Such a distinction, still adhered to in text-books of very recent date, of necessity leads to most incongruous results. Under it the first terms of the homologous series (see p. 264) of saturated hydrocarbons, CH_4 , alcohols, CH_4O , acids, CH_2O_2 , and all their derivatives are classed among mineral substances, while all the higher terms of the same series are organic. Under it urea, CON_2H_4 , the chief product of excretion of the animal body, is a mineral substance, but ethene, C_2H_4 , obtained from the distillation of coal, is organic.

The idea of organic chemistry conveyed by the definition: "that branch of the science of chemistry which treats of the carbon compounds containing hydrogen," is still more fantastic. Under it hydrocyanic acid, CNH , is "organic," but the cyanids, CNK , are "mineral." Oxalic acid, $\text{C}_2\text{O}_4\text{H}_2$, is "organic," and potassium hydroxid, KHO , unquestionably "mineral." If these two act upon each other in the proportion of 90 parts of the former to 56 of the latter, the "organic" monopotassic oxalate, $\text{C}_2\text{O}_4\text{HK}$, is formed, but if the proportion of KHO be doubled, other conditions remaining the same, the "mineral" dipotassic oxalate, $\text{C}_2\text{O}_4\text{K}_2$, is produced. Similarly one of the sodium carbonates, Na_2CO_3 , is "mineral;" the other, NaHCO_3 , is "organic."

The notion that organic substances could only be formed by some mysterious agency, manifested only in organized beings, was finally exploded by the labors of Wöhler and Kolbe. The former obtained urea from ammonium cyanate (1828); while the latter, at a subse-

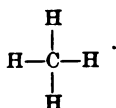
quent period, formed acetic acid, using in its preparation only such unmistakably mineral substances as coal, sulfur, aqua regia, and water. Since Wöhler's first synthesis, chemists have succeeded not only in making from mineral materials many of the substances previously only formed in the laboratory of nature, but have also produced a vast number of carbon compounds which were previously unknown, and which, so far as we know, have no existence in nature.

At the present time, therefore, *we must consider as an organic substance any compound containing carbon, whatever may be its origin and whatever its properties.*

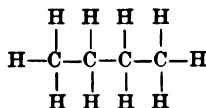
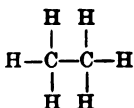
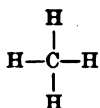
Organic chemistry is, therefore, simply the chemistry of the carbon compounds. In the study of the compounds of the other elements, we have to deal with a small number of substances, relatively speaking, formed by the union with each other of a large number of elements. With the organic substances the reverse is the case. Although compounds have been formed which contain C along with each of the other elements, the great majority of the organic substances are made up of C, combined with a very few other elements; H, O, and N occurring in them most frequently.

It is chiefly in the study of the carbon compounds that we have to deal with radicals (see p. 84). Among mineral substances there are many whose molecules consist simply of a combination of two atoms. Among organic substances there is none which does not contain a radical: indeed, organic chemistry has been defined as "the chemistry of compound radicals."

The atoms of carbon possess in a higher degree than those of any other element the power of uniting with each other, and in so doing of interchanging valences. Were it not for this property of the C atoms, we could have but one saturated compound of carbon and hydrogen, CH₄, or expressed graphically:



There exist, however, a great number of such compounds, which differ from each other by one atom of C and two atoms of H. In these substances the atoms of C may be considered as linked together in a continuous chain, their free valences being satisfied by H atoms, thus:



Homologous Series.—It will be observed that these formulæ differ from each other by CH_2 , or some multiple of CH_2 , more or less. In examining numbers of organic substances which are closely related to each other in their properties, we find that we can arrange the great majority of them in series, each term of which differs from the one below it by CH_2 ; such a series is called an **homologous series**. It will be readily understood that such an arrangement in series vastly facilitates the remembering of the composition of organic bodies. In the following table, for example, are given the saturated hydrocarbons, and their more immediate derivatives. At the head of each vertical column is an **algebraic formula**, which is the **general formula** of the entire series below it; n being equal to the numerical position in the series.

HOMOLOGOUS SERIES.

Saturated hydrocarbons, $\text{C}_n\text{H}_{2n+2}$	Alcohols, $\text{C}_n\text{H}_{2n+2}\text{O}$	Aldehydes $\text{C}_n\text{H}_{2n}\text{O}$	Acids, $\text{C}_n\text{H}_{2n}\text{O}_2$	Ketones, $\text{C}_n\text{H}_{2n}\text{O}$
CH_4	CH_3O	CH_2O	CO_2H_2	
C_2H_6	$\text{C}_2\text{H}_5\text{O}$	$\text{C}_2\text{H}_4\text{O}$	$\text{C}_2\text{O}_2\text{H}_4$	
C_3H_8	$\text{C}_3\text{H}_7\text{O}$	$\text{C}_3\text{H}_6\text{O}$	$\text{C}_3\text{O}_2\text{H}_6$	$\text{C}_3\text{H}_6\text{O}$
C_4H_{10}	$\text{C}_4\text{H}_9\text{O}$	$\text{C}_4\text{H}_8\text{O}$	$\text{C}_4\text{O}_2\text{H}_8$	$\text{C}_4\text{H}_8\text{O}$
C_5H_{12}	$\text{C}_5\text{H}_{11}\text{O}$	$\text{C}_5\text{H}_{10}\text{O}$	$\text{C}_5\text{O}_2\text{H}_{10}$	$\text{C}_5\text{H}_{10}\text{O}$
C_6H_{14}	$\text{C}_6\text{H}_{13}\text{O}$	$\text{C}_6\text{H}_{12}\text{O}$	$\text{C}_6\text{O}_2\text{H}_{12}$	
C_7H_{16}	$\text{C}_7\text{H}_{15}\text{O}$	$\text{C}_7\text{H}_{14}\text{O}$	$\text{C}_7\text{O}_2\text{H}_{14}$	
C_8H_{18}	$\text{C}_8\text{H}_{17}\text{O}$	$\text{C}_8\text{H}_{16}\text{O}$	$\text{C}_8\text{O}_2\text{H}_{16}$	
C_9H_{20}	$\text{C}_9\text{H}_{19}\text{O}$		$\text{C}_9\text{O}_2\text{H}_{18}$	
$\text{C}_{10}\text{H}_{22}$	$\text{C}_{10}\text{H}_{21}\text{O}$		$\text{C}_{10}\text{O}_2\text{H}_{20}$	
$\text{C}_{11}\text{H}_{24}$				
$\text{C}_{12}\text{H}_{26}$			$\text{C}_{12}\text{O}_2\text{H}_{24}$	
$\text{C}_{13}\text{H}_{28}$				
$\text{C}_{14}\text{H}_{30}$			$\text{C}_{14}\text{O}_2\text{H}_{28}$	

But the arrangement in homologous series does more for us than this. The properties of substances in the same series are similar, or vary in regular gradation according to their position in the series. Thus, in the series of monoatomic alcohols (see above) each member yields on oxidation, first an aldehyde, then an acid. Each yields a series of compound ethers by the action of acids upon it. The boiling-points of ethylic alcohol and its seven superior homologues are: 78.3° , 97.4° , 116.8° , 137° , 157° , 176° , 195° , from which it will be seen that the boiling-point of any one of them can be determined, with a maximum error of less than 1° , by taking the mean of those of its neighbors above and below. In this way we may predict, to some extent, the properties of a wanting member in a series before its discovery.

The terms of any homologous series must all have the same con-

stitution, i. e., their constituent atoms must be similarly arranged within the molecule. (See p. 84.)

Isomerism—Metamerism—Polymerism.—*Two substances are said to be isomeric, or to be isomeres of each other, when they have the same percentage composition.* If, for instance, we analyze acetic acid, formic aldehyde and methyl formate, we find that each body consists of C, O and H, in the following proportions:

Carbon	40	=	12
Oxygen	53.33	=	16
Hydrogen	6.67	=	2
	100.00		30

This identity of percentage composition may occur in two ways. The three substances may each contain the same number of each kind of atom in a molecule; or they may contain in their several molecules the same kinds of atoms in multiple proportions. In the above example each substance may have the formula, CH_2O ; or one may have that formula and the others, $\text{C}_2\text{H}_4\text{O}_2$, $\text{C}_3\text{H}_6\text{O}_3$, $\text{C}_4\text{H}_8\text{O}_4$, $\text{C}_5\text{H}_{10}\text{O}_5$, etc.

When two or more substances have the same percentage composition and the same molecular weight they are said to be metameric. When they have the same percentage composition and their molecular weights are simple multiples of the lowest molecular weight represented by that percentage composition, they are said to be polymeric.

Other conditions of isomerism will be considered later (see space isomerism, p. 311, and place isomerism, pp. 339, 436).

In order to determine the composition (the empirical formula) of an organic substance, two factors are therefore necessary: the percentage composition and the molecular weight.

Elementary Organic Analysis.—The first step in an analysis to determine the composition of an organic substance is a qualitative analysis to identify the elements existing in the molecule. This having been done, the quantitative analysis is next in order.

The simplest case is where the substance is a hydrocarbon, i. e., a compound of carbon and hydrogen only. The determination of both elements is made in one operation, by taking advantage of the fact that when a compound containing carbon and hydrogen is heated with cupric oxid all the carbon is converted into CO_2 , and all the hydrogen into H_2O . Thus, if $\text{C}_2\text{H}_6\text{O} + 6\text{CuO} = 2\text{CO}_2 + 3\text{H}_2\text{O} + 6\text{Cu}$, 46 parts of alcohol will produce 88 pts. of carbon dioxid and 54 pts. of water. The apparatus required consists of a tube of difficultly fusible glass, called a combustion tube, about 60 cent. long, drawn out to a point and closed at one end, a "combustion furnace," in which this tube may be heated, and the absorbing apparatus referred to below.

A weighed quantity of the substance of which a "combustion" is to be made (sealed in a small glass bulb if liquid) is placed in the closed end of the combustion tube, *a* Fig. 39, along with the requisite quantity of recently ignited cupric oxid, leaving space for the passage of the gases produced. The tube is then placed in the furnace and its open end connected with a U tube, *b*, filled with fused CaCl_2 , or with fragments of pumice moistened with concentrated H_2SO_4 , whose weight has been determined, and whose purpose it is to absorb the H_2O produced. This first U tube is connected with a "Liebig's bulb" containing a strong solution of KHO , *c*, and this in turn with another U tube in all respects similar to the first, *d*, both *c* and *d* having been previously weighed. The purpose of *c* is to absorb the CO_2 produced, that of *d* to retain water carried over from *c* by the current of gas. The combustion tube is then carefully heated until the evolution of gases ceases, when the closed, drawn-out end of the tube is broken and connected with a gasometer containing pure, dry oxygen, a cur-

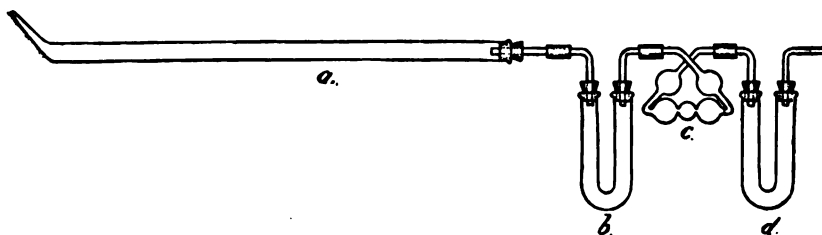


FIG. 39.

rent of which is passed slowly through the apparatus to bring the last portions of the products of combustion into the absorbing apparatus. Finally the U tubes and the KHO bulb are again weighed. The increase in weight of *b* is the weight of H_2O produced, every 9 parts of which represent 1 part of H. The increase in weight of *c* and *d* is the weight of CO_2 produced, every 44 parts of which represent 12 parts of C. If the substance analyzed contain N, Cl, Br or I, a heated column of pure metallic Cu is interposed toward the open end of the combustion tube, to reduce any oxides of N produced to N, and to retain the Cl, Br or I. If the substance contain S, a layer of lead peroxid is similarly placed to retain the S as PbSO_4 .

If the substance consist of C, H and O, the C and H are determined in the manner above described, and the difference between the sum of their weights and that of the substance burnt is the amount of O.

Nitrogen is most readily determined by the method of Kjeldahl. A known weight of the substance is dissolved by heating it in concentrated H_2SO_4 . Potassium permanganate is then added until the mix-

ture is green. The N contained in the substance is thus converted into ammonia. The strongly acid liquid is diluted, rendered alkaline by addition of NaHO, and the NH_3 is distilled over into a receiver containing a known quantity of acid. The amount of NH_3 produced is calculated from the amount of acid neutralized, and every 17 parts of NH_3 represent 14 parts of N. In the analysis of nitro- and cyanogen compounds sugar is added, and in that of nitrates, benzoic acid.

Two other methods of determining N are in general use: That of Dumas, in which the substance is burnt in a manner very similar to that above described, and the N produced is collected and measured. The weight of N is then calculated from the volume, with the necessary corrections for variations of temperature and pressure. In the method of Will and Varrentrap the N of the compound is converted into NH_3 by heating with a caustic alkali, and the amount of NH_3 is determined as in Kjeldahl's method. For the details of these processes and for methods of determination of other elements in organic compounds the student is referred to works on quantitative analysis, such as that of Fresenius. The details of the directions must be rigidly observed to avoid error.

Determination of Molecular Weights.—The percentage composition having been determined, the simplest corresponding ratio of the atoms in the molecule is obtained by dividing the percentage of each element by its atomic weight. Thus if analyses be made of formic aldehyde, acetic acid, methyl formate, lactic acid and glucose, the results in each case will be:

Carbon	40.00 per cent.	$\div 12 = 3.33 = 1$
Hydrogen	6.67 " "	$\div 1 = 6.67 = 2$
Oxygen	53.33 " "	$\div 16 = 3.33 = 1$

and the simplest empirical formula of all of the substances mentioned is therefore CH_2O . The molecular weight of formic aldehyde is 30; its formula is therefore CH_2O ($12+2+16$). The molecular weights of acetic acid and of methyl formate are 60; they, therefore, each have the formula $\text{C}_2\text{H}_4\text{O}_2$. The molecular weight of lactic acid is 90 and that of glucose 180; the formula of the former is, therefore, $\text{C}_3\text{H}_6\text{O}_3$, and that of the latter $\text{C}_6\text{H}_{12}\text{O}_6$.

If the substance be one which can be vaporized without decomposition, its molecular weight is derived from its specific gravity as referred to hydrogen in the manner already described (p. 56). The process for determining the specific gravity now generally adopted is that of Victor Meyer. (See Ganot's Physics, 15th Am. Ed., p. 381, or other works upon that subject.) If the substance be one which cannot be vaporized without decomposition, its molecular weight may usually be determined by the freezing or boiling point methods

referred to on pp. 68, 69. In some cases neither of these physical methods are applicable. Then chemical methods must be resorted to. These consist in producing derivatives, which are then analyzed and the results thus obtained compared with the formulæ deducible from the analysis of the original compound. These methods are sometimes exceedingly complicated, in other cases very simple. When the substance is a base or an acid it is converted into a mineral ester or into a salt, and the combined mineral acid or metal is determined. For example: Acetic acid and lactic acid both have the percentage composition C=40.00 per cent, H=6.67 per cent, O=53.33 per cent, corresponding to the formula CH_2O , or some multiple thereof. The atomic weight of silver is 107.7. If the two acids are converted into their silver salts, and the amount of silver in each determined, the acetate will be found to contain 64.6 per cent of silver, and the lactate 54.8 per cent. If both acids are monobasic the former percentage of silver corresponds to the formula $\text{C}_2\text{H}_3\text{O}_2\text{Ag}$, and the latter to the formula $\text{C}_3\text{H}_5\text{O}_3\text{Ag}$. The basicity of the acid is determined from the increase of molecular conductivity of solutions of its sodium salt on dilution, by the method referred to on p. 75.

Determination of Constitution.—The identity and properties of organic compounds depend not only upon their *composition*, i. e., the number and kind of atoms composing the molecule, but also upon their *constitution*, i. e., the arrangement of the atoms in the molecule (see p. 84). The constitution of a substance is determined by a study of the methods of its formation, of the products of its decomposition, and of the substances produced by the introduction of other elements or groups into its molecule. A statement of the more important principles, and one or two examples, must suffice here, the subject being further developed in the sequel.

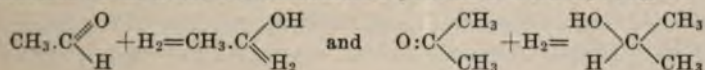
The carbon atom is quadrivalent in almost all, if not in all organic compounds. In the few in which it is considered as bivalent, as in carbon monoxid, CO , and the isonitrils, $(\text{C}_2\text{H}_5)\text{—N}=\text{C}$, the oxygen may be considered to be quadrivalent, and the nitrogen quinquivalent, in which case the carbon would be quadrivalent.

The carbon atoms may unite with each other in three ways: (1) Two carbon atoms may exchange a single valence in their union, forming a hexavalent group, $\equiv\text{C}\text{—}\text{C}\equiv$; (2) they may unit with exchange of two valences, forming a quadrivalent group, $=\text{C}=\text{C}=$; or, (3) they may unite with exchange of three valences, forming a bivalent group, $\text{—C}\equiv\text{C—}$. These are referred to as **single, double and treble linkages**, respectively.

Those compounds in which all of the linkages are single, and in which all of the possible valences of the constituent atoms are satisfied are **saturated compounds**. No other atom or radical can be intro-

duced into a saturated molecule except by **substitution**, i. e., by causing the introduced atom or radical to take the place of some other, or others, of equivalent valence, simultaneously removed. Thus, when chloroform (itself a substituted derivative of marsh gas, CH_4) is converted into carbon tetrachlorid, the remaining hydrogen is removed as hydrochloric acid: $\text{CHCl}_3 + \text{Cl}_2 = \text{CCl}_4 + \text{HCl}$.

Only such substances as contain two carbon atoms doubly or trebly linked, $=\text{C}=\text{C}=$ or $-\text{C}\equiv\text{C}-$, are usually considered as **unsaturated compounds**. Such compounds may be modified both by substitution and by **addition**, i. e., by breaking out the double or treble linkages and the introduction of two new univalents, or one bivalent, for each linkage so liberated. Thus, ethylene yields ethylene chlorid by addition: $\text{H}_2\text{C}:\text{CH}_2 + \text{Cl}_2 = \text{ClH}_2\text{C}.\text{CH}_2\text{Cl}$; or, by substitution and addition, carbon hexachlorid: $\text{H}_2\text{C}:\text{CH}_2 + 5\text{Cl}_2 = \text{Cl}_3\text{C}.\text{CCl}_3 + 4\text{HCl}$. (See also pp. 273, 284.) But compounds in which all of the carbon atoms are singly interlinked may also form products of addition, and in this sense are unsaturated, if they contain a double linkage between a carbon atom and a bivalent. Thus, the aldehydes and ketones form alcohols as addition products with hydrogen:



In the reactions referred to above in which chlorine is substituted for hydrogen, it is not only added to the molecule operated upon, but also removes hydrogen by combining with it, and hence two atoms of chlorine are required for each atom of hydrogen removed. Similarly, when O removes H_2 , in oxidations, two atoms of oxygen are required for each two atoms of hydrogen removed, as when alcohol is oxidized to acetic acid: $\text{C}_2\text{H}_6\text{O} + \text{O}_2 = \text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O}$. Consequently in oxidations an even number of hydrogen atoms is always removed. The tendency to the formation of water is so strong that in reactions in which two or more hydroxyl groups should unite with the same carbon atom, water almost invariably splits off and oxygen unites doubly with the carbon. Thus caustic potash does not act upon ethidene chlorid to produce a glycol according to the equation $\text{CH}_3.\text{CHCl}_2 + 2\text{KHO} = \text{CH}_3.\text{CH}(\text{OH})_2 + 2\text{KCl}$, but to produce an aldehyde according to the equation, $\text{CH}_3.\text{CHCl}_2 + 2\text{KHO} = \text{CH}_3.\text{CHO} + \text{H}_2\text{O} + 2\text{KCl}$.

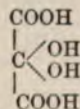
Exceptions to this rule occur when the carbon atom is linked to another carbon atom contained in a highly oxidized or halid group, as in the compounds:



Glyoxalic acid.



Chloral hydrate.



Mesoxalic acid.

Usually when an atom or group replaces another in a compound it occupies the position vacated by that which is removed, as when alcohol is formed by the action of caustic potash upon ethyl iodid: $\text{CH}_3.\text{CH}_2\text{I} + \text{KHO} = \text{CH}_3.\text{CH}_2\text{OH} + \text{KI}$. There is an exception to this rule when an unsaturated compound may yield either another unsaturated compound in obedience to the rule or an isomeric saturated compound in violation to it, the more stable saturated compound is formed. Thus the hydration of vinyl bromid, $\text{CH}_2:\text{CHBr}$, does not produce vinyl alcohol, $\text{CH}_2:\text{CHOH}$, but its isomere: aldehyde, $\text{CH}_3.\text{CHO}$. Indeed, unsaturated compounds are frequently converted into saturated isomeres by intramolecular transposition of atoms by mere application of heat.

The genesis of ethylic alcohol from the action of caustic potash upon ethyl iodid: $\text{CH}_3.\text{CH}_2\text{I} + \text{KHO} = \text{CH}_3.\text{CH}_2\text{OH} + \text{KI}$, shows that the alcohol contains the univalent group CH_2OH , which, on oxidation, may lose two atoms of hydrogen with formation of either one of the two univalent groups CHO , or COOH ; which occur in the products of oxidation of ethylic alcohol: aldehyde and acetic acid.

The groups CH_2OH , CHO and COOH , referred to above, are examples of the so-called **characterizing groups** which exist in the molecules of different classes of substances. The following are the more commonly recurring characterizing groups, and the classes of substances in which they occur:

$(\text{CH}_2\text{OH})'$	$= \begin{array}{c} \text{H} \\ \diagup \\ \text{HO} \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{H} \end{array}$	in primary alcohols, called <i>methoxyl</i> ,
$(\text{CHOH})''$	$= \begin{array}{c} \text{H} \\ \diagup \\ \text{HO} \end{array} \text{C} =$	“ secondary alcohols,
$(\text{COH})'''$	$= :\text{C}.\text{OH}$	“ tertiary alcohols,
$(\text{CHO})'$	$= \text{O}=\text{C} \begin{array}{c} \diagdown \\ \text{H} \end{array}$	“ aldehydes,
$(\text{CO})''$	$= \text{O}:\text{C}:$	“ ketones, called <i>carbonyl</i> ,*
$(\text{COOH})'$	$= \text{O}=\text{C} \begin{array}{c} \diagdown \\ \text{OH} \end{array}$	“ acids, called <i>carboxyl</i> ,
$(\text{SO}_3\text{OH})'$	$= \begin{array}{c} \text{O} \\ \diagup \\ \text{O} \end{array} \text{S} \begin{array}{c} \diagdown \\ \text{OH} \end{array}$	“ sulfonic acids,
$(\text{SO}_2)''$	$= \begin{array}{c} \text{O} \\ \diagup \\ \text{O} \end{array} \text{S} =$	“ sulfones,
$(\text{NH}_2)'$	$= \text{H}_2:\text{N}.$	“ amido compounds,
$(\text{NH})''$	$= \text{H}.\text{N}:$	“ imido compounds,
$(\text{NO}_2)'$	$= \begin{array}{c} \text{O} \\ \diagup \\ \text{O} \end{array} \text{N}-$	“ nitro compounds,
$(\text{NO})'$	$= \text{O}:\text{N}.$	“ nitroso compounds.

*This group also exists in other compounds, as in the aldehydes and acids in the manner indicated in the text, and in compounds, such as carbonyl chlorid, COCl_2 , urea, $\text{NH}_2.\text{CO}.\text{NH}_2$, etc.

Nomenclature of Organic Compounds.—The vast number and great variety of structure of organic compounds make it difficult to devise a system of nomenclature which will apply to the more complex derivatives without producing names which are most complicated and difficult of pronunciation. Indeed, in view of the constantly increasing number of carbon compounds, no complete system of nomenclature is as yet possible. The most recent attempt to formulate one is that of the Geneva Commission of 1892. In this system the names of the hydrocarbons serve as the roots from which the names of their derivatives are constructed by the addition of syllables indicating the function (see p. 63) of the substance. Thus the alcohols are indicated by the syllable *ol*, the aldehydes by *al*, the ketones by *on*, and the acids by the word *acid*. The "Geneva" name of ethylic alcohol would be *ethanol*, that of acetic aldehyde *ethanal* and that of acetic acid *ethan-acid*. These names have not come into general use.

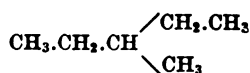
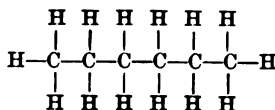
In the nomenclature generally followed the name of a substance is made up of the name of that of the class, or "function," to which the substance belongs, as *acid*, *alcohol*, *ketone*, *ester*, etc., to which are added a qualifying word derived from the origin of the body, as *lactic acid*, *acetic acid*, etc., or from its composition, as *methylic alcohol*, *ethylic ether*, etc., and the names of any radicals which have been introduced into the molecule of the parent compound. Thus the name of the substance $\text{COOH} \cdot \text{CH}_2 (\text{NH} \cdot \text{CH}_3)$ is *methyl-amido-acetic acid*, in which "*acetic acid*" indicates that it is derived from acetic acid, $\text{COOH} \cdot \text{CH}_3$, the syllable *amido* that NH_2 has been substituted for H in the CH_3 of the acid, and *methyl* that CH_3 has been substituted for H in NH_2 .

The names of the univalent radicals terminate in *yl*, as *methyl* $(\text{CH}_3)'$, *ethyl* $(\text{C}_2\text{H}_5)'$, *acetyl* $(\text{C}_2\text{H}_3\text{O})'$, etc. Those of bivalent radicals terminate in *ene*, as *methylene*, $(\text{CH}_2)''$, *ethidene* $(\text{C}_2\text{H}_4)''$, etc., and those of the trivalent radicals in *enyl* or in *ine*, as *methenyl* or *methine* $(\text{CH})'''$, *ethenyl* or *ethine* $(\text{C}_2\text{H}_3)'''$, etc.

Classification of the Carbon Compounds.—The hydrocarbons, consisting of carbon and hydrogen only, constitute the framework of the classification adopted, all other carbon compounds being considered as derivable from the hydrocarbons by substitution or by addition.

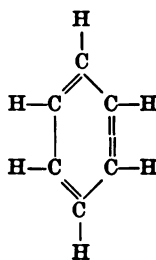
Carbon compounds are divided into two great classes, differentiated by the manner in which the carbon atoms are linked together:

A. OPEN CHAIN COMPOUNDS, also called *acyclic*, *fatty*, or *aliphatic* ($\alpha\lambda\epsilon\iota\phi\alpha\rho$ =fat) compounds. In these compounds the carbon atoms are attached to each other in an open or arborescent chain, in which two or more carbon atoms are linked to but one other carbon atom, as in the compounds:

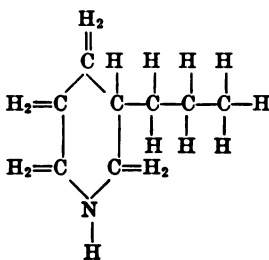


In the hydrocarbons of this class the number of hydrogen atoms, or this number, plus the number of univalent atoms that can be introduced into the molecule by addition, is equal to twice the number of carbon atoms plus two.

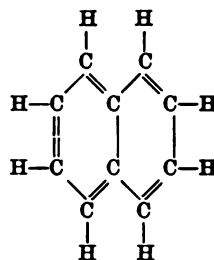
B. CLOSED CHAIN COMPOUNDS, also called *cyclic* or *aromatic* compounds. These compounds contain one or more closed *chains*, *rings*, or *nuclei* in which each carbon atom is linked to at least two other carbon atoms, or their equivalent, as in the compounds:



Benzene.



Coniïn.



Naphthalene

The closed chain compounds are subdivided into two classes:

I. *Carbocyclic compounds*, in which the ring or rings consist of carbon atoms exclusively, as in benzene and naphthalene, and

II. *Heterocyclic compounds*, in which atoms of elements other than carbon enter into the composition of the ring, as in coniïn.

OPEN CHAIN, ALIPHATIC, ACYCLIC OR FATTY COMPOUNDS.

HYDROCARBONS.

Six series are known:

A. Methane, or Paraffin Series. These are saturated compounds and have the algebraic formula, C_nH_{2n+2} . Their names terminate in "ane," e. g., Butane, $CH_3.CH_2.CH_2.CH_3$.

B. Olefin Series, containing two doubly-linked carbon atoms. General formula C_nH_{2n} . Their names terminate in "ene," e. g., Butene, $CH_2:CH.CH_2.CH_3$.

C. Acetylene Series, containing two trebly-linked carbon atoms. Algebraic formula, C_nH_{2n-2} . Their names terminate in "ine," e. g., Propine, $CH:C.CH_3$.

D. Diolefin Series, containing two pairs of doubly-linked carbon atoms. Algebraic formula, C_nH_{2n-2} , isomeric with the members of the acetylene series. Their names terminate in "diene," e. g., Propadiene, $CH_2:C:CH_2$.

E. Olefin-acetylene Series, containing both doubly- and trebly-linked carbon atoms. General formula, C_nH_{2n-4} . Their names terminate in "one," eg., Butone, $H_2C:CH.C:CH$.

F. Diacetylene Series, containing two pairs of trebly-linked carbon atoms. Algebraic formula, C_nH_{2n-6} . Their names are constructed by prefixing the syllable "di" to the name of the hydrocarbon of series C, from which they are derivable by fusion and elimination of H_2 or its equivalent, e. g., Diacetylene, $HC:C:C:CH$. The sixth terms, of which there are two isomeres: Dipropargyl, $HC:C.CH_2.CH_2.C:CH$, and Dimethyl diacetylene, $H_3C.C:C:C:C.CH_3$, are isomeric with benzene, the most important of the closed chain hydrocarbons.

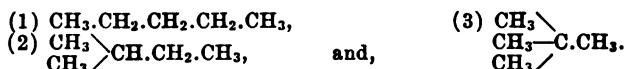
SATURATED COMPOUNDS—METHANE SERIES.

HYDROCARBONS.

The saturated hydrocarbons at present known extend in unbroken series from methane, CH_4 , to tetracosane, $C_{24}H_{50}$; and above that some members are known as high as dimyricyl, $C_{60}H_{122}$. The algebraic formula of the series is C_nH_{2n+2} . They are called **paraffins** because of their great stability (*parum*=little, *affinis*=affinity); and

also **alkanes**. They are also considered as the **hydrides** of the alcoholic radicals, C_nH_{2n+1} , methyl, ethyl, etc., which are called **alkyls**.

In the higher terms of the series, above the third, there exist two or more isomeres, increasing progressively in number with an increasing number of carbon atoms. Thus there are three having the empirical formula, C_5H_{12} :



Hydrocarbons and their derivatives having the "unbranched" structure shown in formula (1) above, are designated as "normal" compounds; those derived from (2) are called "iso" compounds; and those derived from (3) "meso" compounds.

The number of possible isomeres increases rapidly with an increasing number of carbon atoms. It has been calculated that the number of possible isomeres with increasing values of n are as follows:

$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$
1	1	1	2	3	5
$n = 7$	$n = 8$	$n = 9$	$n = 10$	$n = 11$	$n = 12$
9	18	35	75	159	357

Many of these hydrocarbons exist in nature, in petroleum, and in the gases accompanying it. They may be produced by the following **general reactions**:

(1) By the action of finely-divided zinc, silver or copper, or of sodium either alone, at elevated temperatures, or in the presence of H_2O , upon the corresponding iodids: $2C_2H_5I + Zn \rightarrow ZnI_2 + C_2H_6$, or, $2C_2H_5I + Na_2 \rightarrow 2NaI + C_4H_{10}$.

(2) By electrolysis of the corresponding fatty acid: $2C_2H_4O_2 \rightarrow 2CO_2 + C_2H_6 + H_2$.

(3) By the action of the organo-zincic derivative upon the iodid of the alcoholic radical, upon the corresponding olefin iodid, or upon the allylic iodid (p. 426).

(4) By the action of highly concentrated hydriodic acid at 275° – 300° (527° – 572° F.) upon hydrocarbons of the ethene and ethine series, upon alcohols, amins, etc. This is a method of hydrogenation applicable in many other cases. See p. 136.

(5) By the destructive distillation of many organic substances.

General Properties.—They are gaseous, liquid, or solid, and have sp. gr. and boiling points increasing with the number of C atoms. The first four members are gaseous at the ordinary temperature, those above $C_{15}H_{32}$ are crystalline solids; the intermediate ones are colorless liquids. They are lighter than H_2O , neutral, insoluble in H_2O ,

soluble in alcohol, ether, and in liquid hydrocarbons. Their odor is faint and not unpleasant.

Chlorin and bromin decompose them, with formation of products of substitution. They are inflammable and burn with a luminous flame. Nitric acid forms nitro-derivatives with the higher terms.

The formulæ given above (p. 274) show that these hydrocarbons are made up of groups: —HC_3 , called **methyl**, =CH_2 , **methylene**, ≡CH , **methenyl** or **methine**, and ≡C atoms, all of the free valences of each of which are satisfied by attachment to other C atoms. In the molecular structure of their derivatives, these several fractions of the hydrocarbons are modified, according to their valence-capacity, by substitution or by interpolation. Thus, by substitution the groups: —CHBr_2 , =CO , and ≡CCl are derived from —CH_3 , =CH_2 , and ≡CH respectively, and by interpolation the groups $\text{—CH}_2\text{OH}$, =CHOH , and ≡COH .

Methyl Hydrid—Methane—Marsh-gas—Light carburetted hydrogen—Fire-damp— CH_4 —16—is given off in swamps as a product of decomposition of vegetable matter, in coal mines, and in the gases issuing from the earth in the vicinity of petroleum deposits. It is also formed during putrefaction of protein bodies and fermentation of carbohydrates. From these origins it exists in intestinal gases, sometimes to the extent of 26.5 per cent. Coal-gas contains it in the proportion of 36–50 per cent. It may be prepared by strongly heating a mixture of sodium acetate with sodium hydroxid and quicklime. Its complete synthesis, which is of theoretic interest, may be effected in several ways: (1) Carbon disulfid is first produced by passing vapor of sulfur over coal, heated to redness: $\text{C} + \text{S}_2 = \text{CS}_2$. This may either be passed, along with hydrogen sulfid, over red-hot copper, when: $\text{CS}_2 + 2\text{H}_2\text{S} + 8\text{Cu} = \text{CH}_4 + 4\text{Cu}_2\text{S}$, or, (2) it may be converted into carbon tetrachlorid by the reaction: $\text{CS}_2 + 3\text{Cl}_2 = \text{CCl}_4 + \text{S}_2\text{Cl}_2$; and this reduced by nascent hydrogen: $\text{CCl}_4 + 4\text{H}_2 = \text{CH}_4 + 4\text{HCl}$. (3) Carbon monoxid, prepared by heating carbon in a limited quantity of air, is reduced by hydrogen when the two are treated with the induced electric current: $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$. (4) Aluminium carbid is decomposed by water according to the equation: $\text{C}_3\text{Al}_4 + 12\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2(\text{OH})_6$.

It is a colorless, odorless, tasteless gas; very sparingly soluble in H_2O ; sp. gr. 0.559A. At high temperatures, it is decomposed into C and H. It burns in air with a pale yellow flame. Mixed with air or O it explodes violently on contact with flame, producing water and carbon dioxid; the latter constituting the **after-damp** of miners. It is not affected by Cl in the dark, but, under the influence of diffuse daylight, one or more of the H atoms are displaced by an equivalent quantity of Cl. In direct sunlight the substitution is accompanied by an explosion.

Petroleum.—Crude petroleum varies in color from a faintly yellowish tinge to a dark brown, nearly black, with greenish reflections. The lighter-colored varieties are limpid, and the more highly colored of the consistency of thin syrup. The sp. gr. varies from 0.74 to 0.92. Crude petroleums consist of normal paraffins (the lowest terms of the series being found in the gases accompanying petroleum and held in solution by the oil under the pressure it supports in natural pockets), besides hydrocarbons of the olefin, paraffene, and benzene series. They also contain varying quantities of sulfur compounds, which communicate a disgusting odor to some oils.

The crude oil is highly inflammable, usually highly colored, and is prepared for its multitudinous uses in the arts by the processes of distillation and refining. The products of lowest boiling point are usually consumed, but are sometimes condensed.

The principal products of petroleum are : **Cymogene**, boils at 0° (32° F.), used in ice machines; **Rhigolene**, a highly inflammable liquid, sp. gr. about 0.60, boils at about 20° (68° F.), used to produce cold by its rapid evaporation. **Petroleum ether**, boils at 40° – 70° (104° – 158° F.), used as a solvent. **Gasolene**, boils from 45° (113° F.) to 76° (168.8° F.), used as a fuel and for the manufacture of "air gas." **Naphtha**, divided into three grades, C, B, and A, boils from 82.2° (180° F.) to 148.8° (300° F.), used as a solvent for fats, etc., and in the manufacture of "water gas." Sometimes called "safety oil." **Benzine**, or **benzolene**, boils from 148° (298° F.) to 160° (320° F.), used as a solvent in making paints and varnishes. The most important product of petroleum is that portion which distills between 176° (349° F.) and 218° (424° F.), and which constitutes **kerosene** and other oils used for burning in lamps. An oil to be safely used for burning in lamps should not "flash," or give off inflammable vapor, below 37.4° (100° F.), and should not burn at temperatures below 149° (300° F.). The better grades of kerosene have a flash point of from 110° F. to 150° F.

From the residue remaining after the separation of the kerosene, many other products are obtained. **Lubricating oils**, of too high boiling-point for use in lamps. **Paraffin**, a white, crystalline solid, fusible at 45° – 65° (113° – 149° F.), which is used in the arts for a variety of purposes formerly served by wax, such as the manufacture of candles. In the laboratory it is very useful for coating the glass stoppers of bottles, and for other purposes, as it is not affected by acids or by alkalis. It is odorless, tasteless, insoluble in H_2O and in cold alcohol; soluble in boiling alcohol and in ether, fatty and volatile oils and mineral oils. It is also obtained by the distillation of certain varieties of coal, and is found in nature in **fossil wax** or **ozocerite**.

The products known as **vaseline**, **cosmoline**, etc., are mixtures of paraffin and the heavier petroleum oils. Their consistency depends upon the relative proportion of the higher paraffins, of increasing fusing-point, which they contain, from the oily **petrolatum liquidum** (U. S.), to the hard **petrolatum durum** (U. S.). Like petroleum itself, its various commercial derivatives are not definite compounds, but mixtures of the hydrocarbons of this series.

HALOID DERIVATIVES OF THE PARAFFINS.

By the action of Cl or Br, upon the paraffins, or by the action of HCl, HBr or HI upon the corresponding hydroxids, the monohydric alcohols (p. 286), compounds are obtained in which one of the H atoms of the hydrocarbon has been replaced by an atom of Cl, Br or I: $C_2H_6 + Br_2 = C_2H_5Br + HBr$, or $C_2H_5OH + HCl = C_2H_5Cl + H_2O$. Or they are more readily obtained by the action of the phosphorus halids, or of the halogen in presence of phosphorus upon the monohydric alcohols: $CH_3.CH_2OH + PCl_5 = CH_3.CH_2Cl + POCl_3 + HCl$. These **monohalogen paraffins**, or **haloid ethers**, or **haloid esters** (p. 358), or **alkyl halids**, may also be considered as the chlorids, etc., of the alcoholic radicals, methyl, etc.

These compounds are of great service for the introduction of their alkyls into other molecules. Thus, benzene and methyl chlorid form methyl benzene: $C_6H_6 + CH_3Cl = C_6H_5.CH_3 + HCl$.

Caustic potash or soda in alcoholic solution splits off the halogen and water, with formation of an unsaturated hydrocarbon: $CH_3.CH_2Br + KHO = CH_2:CH_2 + KBr + H_2O$. Heated with aqueous potash the haloid esters produce the corresponding alcohols: $CH_3.CH_2Br + KHO = CH_3.CH_2OH + KBr$. Heated with alcoholic solution of potassium cyanid at 100° , the haloid esters produce the alkyl cyanids: $CH_3.CH_2I + KCN = CH_3.CH_2.CN + KI$ (p. 393). They also combine with ammonia to form amins (p. 379): $CH_3Cl + NH_3 = CH_3.NH_3.Cl$.

By the further action of the halogen upon the paraffin, products of higher substitution are formed. Thus, from methane: methylene chlorid, CH_2Cl_2 , methenyl chlorid, $CHCl_3$, and carbon tetrachlorid, CCl_4 . In the **dihalogen paraffins** above the first the two halogen atoms may be attached either to different or to the same carbon atom. The former class may be considered as the neutral haloid esters of the glycols, or dihydric alcohols (pp. 294, 363): $CH_2Cl_2.CH_2Cl_2$, as the monohalogen paraffins are the haloid esters of the monohydric alcohols. They are obtained by the action of the halogens upon the olefins (p. 424): $CH_2:CH_2 + I_2 = CH_2I.CH_2I$, and from them the glycols are obtained. Those dihalogen paraffins in which the two halogen atoms are attached to the same carbon atom, are known as **aldehyde halids** if the carbon

atom be terminal as in $\text{CH}_3.\text{CH}_2.\text{CHCl}_2$, and as **ketone halids** if it be intermediate, as in $\text{CH}_3.\text{CCl}_2.\text{CH}_3$, from the resemblance of their structure to those of the aldehydes and ketones (pp. 300, 307) respectively, and from the fact that they are obtained by the action of phosphorus halids upon those substances: $\text{CH}_3.\text{CHO} + \text{PCl}_5 = \text{CH}_3.\text{CHCl}_2 + \text{POCl}_3$, and $\text{CH}_3.\text{CO}.\text{CH}_3 + \text{PCl}_5 = \text{CH}_3.\text{CCl}_2.\text{CH}_3 + \text{POCl}_3$. The two classes are also distinguished as **symmetrical** and **unsymmetrical** dihalids.

Nascent hydrogen reduces all of the halogen derivatives to the parent hydrocarbon: $\text{CHCl}_3 + 3\text{H}_2 = \text{CH}_4 + 3\text{HCl}$.

Methyl Chlorid— CH_3Cl —50.5—is a colorless gas, slightly soluble in H_2O , and having a sweetish taste and odor. It is prepared commercially by heating trimethylammonium chlorid (obtained by distilling beet sugar molasses): $3\text{N}(\text{CH}_3)_3\text{HCl} = 2\text{CH}_3\text{Cl} + 2\text{N}(\text{CH}_3)_3 + \text{NH}_2\text{CH}_3 + \text{HCl}$. It may be condensed to a liquid which boils at -22° (-7.6°F.), in which form it is used in ice machines, as a spray in neuralgia, and as an anæsthetic; for the latter uses either alone or mixed with CHCl_3 , $\text{C}_4\text{H}_{10}\text{O}$, or $\text{C}_2\text{H}_5\text{Cl}$. It burns with a greenish flame.

Dichlormethane—**Methene chlorid**—**Methylene chlorid**—**Chloromethyl**—**Monochlormethyl chlorid**— CH_2Cl_2 —85—is obtained by the action of Cl upon CH_4 , and by the reduction of CHCl_3 by nascent hydrogen.

It is a colorless, oily liquid; boils at 40° (104°F.); sp. gr. 1.36; its odor is similar to that of chloroform; it is very slightly soluble in H_2O and is not inflammable. It has been used as an anæsthetic, but has been discarded as being less safe than chloroform.

Trichlormethane—**Methenyl chlorid**—**Formyl chlorid**—**Dichloromethyl chlorid**—**Chloroform**—**Chloroformum** (U. S.; Br.)— CHCl_3 —120.5—is obtained by heating in a capacious still, 35–40 litres (9–11 gall.) of H_2O , adding 5 kilos (11 lbs.) of recently slacked lime and 10 kilos (22 lbs.) of chlorid of lime; 2.5 kilos (4 qts.) of alcohol are then added and the temperature quickly raised until the product begins to distil, when the fire is withdrawn, heat being again applied toward the end of the reaction. The crude chloroform so obtained is purified, first by agitation with H_2SO_4 then by mixing with alcohol and recently ignited potassium carbonate, and distilling the mixture.

Chloroform is now extensively manufactured by the action of bleaching powder upon acetone, the reaction being expressed by the equation: $2\text{CO}(\text{CH}_3)_2 + 6\text{CaCl}(\text{OCl}) = 2\text{CHCl}_3 + 2\text{Ca}(\text{HO})_2 + (\text{CH}_3\text{—COO})_2\text{Ca} + 3\text{CaCl}_2$.

It is best obtained pure by heating chloral hydrate with an alkali: $\text{C}_2\text{HCl}_3(\text{OH})_2 + \text{KHO} = \text{CHCl}_3 + \text{HCOOK} + \text{H}_2\text{O}$.

It is a colorless, volatile liquid, having a strong, agreeable, ether-eal odor, and a sweet taste; sp. gr. 1.497; very sparingly soluble in

H₂O; miscible with alcohol and ether in all proportions; boils at 60.8° (141.4° F.). It is a good solvent for many substances insoluble in H₂O, such as phosphorus, iodine, fats, resins, caoutchouc, gutta-percha and the alkaloids.

It ignites with difficulty, but burns from a wick with a smoky, red flame, bordered with green. It is not acted on by H₂SO₄, except after long contact, when HCl is given off. In direct sunlight Cl converts it into CCl₄ and HCl. The alkalies in aqueous solution do not act upon it, but when heated with them in alcoholic solution, it is decomposed with formation of chlorid and formate of the alkaline metal: $\text{CHCl}_3 + 4\text{KHO} = \text{H.COOK} + 3\text{KCl} + 2\text{H}_2\text{O}$. When perfectly pure it is not altered by exposure to light; but if it contain compounds of N, even in very minute quantity, it is gradually decomposed by solar action into HCl, Cl and other substances. When used as an anæsthetic chloroform should not be colored by agitation with concentrated, colorless sulfuric acid, and should color the latter only faintly yellow, or not at all; and when it is evaporated the remaining film of moisture should have no taste or odor other than those of chloroform.

Analytical Characters.—(1) Add a little alcoholic solution of potash and 2-3 drops of anilin and warm: the disagreeable odor of isobenzonitril (q. v.) is produced. (2) Vapor of CHCl₃, when passed through a red-hot tube, is decomposed with formation of HCl and Cl, the former of which is recognized by the production of a white ppt., soluble in ammonium hydroxid, in an acid solution of silver nitrate. This test does not afford reliable results when the substance tested contains a free acid and chlorids. (3) Dissolve about 0.01 gm. of β naphthol in a small quantity of KHO solution, warm, and add the suspected liquid; a blue color is produced. (4) Add about 0.3 gm. resorcinol in solution, and 3 gtt. NaHO solution and boil strongly. In the presence of CHCl₃ a yellowish-red color is produced, and the liquid exhibits a beautiful yellow-green fluorescence.

Toxicology.—The action of chloroform varies as it is taken by the stomach or by inhalation. In the former case, owing to its insolubility, but little is absorbed, and the principal action is the local irritation of the mucous surfaces. Recovery has followed a dose of four ounces, and death has been caused by one drachm, taken into the stomach. Chloroform vapor acts much more energetically, and seems to owe its potency for evil to its paralyzing influence upon the respiratory nerve centers, and upon the cardiac ganglia. While persons suffering from heart disease are particularly susceptible to the paralyzing effect of chloroform vapor, there are many cases recorded of death from the inhalation of small quantities, properly diluted, in which no heart lesion was found upon a post-mortem examination. Chloroform is apparently not altered in the system.

No chemical antidote for chloroform is known. When it has been swallowed, stomach-lavage and emetics are indicated; when taken by inhalation, a free circulation of air should be established about the face; artificial respiration and the application of the induced current to the sides of the neck and epigastrium should be resorted to.

The nature of the poison is usually revealed at the autopsy by its peculiar odor, which is most noticeable on opening the cranial and thoracic cavities. In a toxicological analysis, chloroform is to be sought for especially in the lungs and blood. These are placed in a flask; if acid, neutralized with sodium carbonate, and subjected to distillation at the temperature of the water-bath. The vapors are passed through a tube of difficultly fusible glass; at first the tube is heated to redness for about an inch of its length, and test No. 2 applied to the issuing gas. The tube is then allowed to cool, and the distillate collected in a pointed tube, from the point of which any CHCl_3 is removed by a pipette and tested according to Nos. 1, 3 and 4 above.

Carbon Tetrachlorid—*Chlorocarbon*— CCl_4 —154—is formed by the prolonged action, in sunlight, of Cl upon CH_3Cl or CHCl_3 ; or more rapidly, by passing Cl, charged with the vapor of carbon disulfid, through a red-hot tube, and purifying the product.

It is a colorless, oily liquid, insoluble in H_2O ; soluble in alcohol and in ether; sp. gr. 1.56; boils at 78° (172.4°F.). Its vapor is decomposed at a red heat into a mixture of the dichlorid, C_2Cl_4 , trichlorid, C_2Cl_6 , and free Cl.

Methyl Bromid— CH_3Br —95.—A colorless liquid; sp. gr. 1.664; boils at 13° (55.4°F.); formed by the combined action of P and Br on methyl hydroxid.

Tribrommethane—*Dibromomethyl bromid*—*Methenyl bromid*—*Formyl bromid*—**Bromoform**— CHBr_2 .Br—253—is prepared by gradually adding Br to a cold solution of KHO in methyl alcohol until the liquid begins to be colored; and rectifying over CaCl_2 .

A colorless, aromatic, sweet liquid; sp. gr. 2.13; boils at 150° – 152° (302° – 306°F.); solidifies at -9° (15.8°F.); sparingly soluble in H_2O ; soluble in alcohol and ether. Boiled with alcoholic KHO it is decomposed in the same way as is CHCl_3 .

Its physiological action is similar to that of CHCl_3 . It occurs as an impurity of commercial Br, accompanied by carbon tetrabromid, CBr_4 .

Methyl Iodid— CH_3I —142—a colorless liquid, sp. gr. 2.237; boils at 45° (113°F.); burns with difficulty, producing violet vapor of iodine. It is prepared by a process similar to that for obtaining the bromid, and is used in the anilin industry.

Triiodomethane—*Diiodomethyl iodid*—*Methenyl iodid*—*Formyl*

iodid—**Iodoform**—**Iodoformum**, U. S.— CHI_3 —394.—Formed like CHCl_3 and CHBr_3 , by the combined action of KHO and the halogen upon alcohol; it is also produced by the action of I upon a great number of organic substances, and is usually prepared by heating a mixture of alkaline carbonate, H_2O , I and ethylic alcohol, and purifying the product by recrystallization from alcohol. It is also produced from acetone by making a solution containing 50 gm. KI , 6 gm. acetone, and 2 gm. NaHO in 2 L. H_2O and gradually adding a dilute solution of KClO_3 .

Iodoform is a solid, crystallizing in yellow, hexagonal plates, which melt at 120° (248°F.). It may be sublimed, a portion being decomposed. It is insoluble in water, acids and alkaline solutions; soluble in alcohol, ether, carbon disulfid, and the fatty and essential oils; the solutions, when exposed to the light, undergo decomposition and assume a violet-red color. It has a sweet taste, and a peculiar, penetrating odor, resembling, when the vapor is largely diluted with air, that of saffron. When heated with potash a portion is decomposed into formate and iodid, while another portion is carried off unaltered with the aqueous vapor. It contains 96.7% of its weight of iodin.

Ethyl Chlorid—*Hydrochloric or muriatic ether*— $\text{C}_2\text{H}_5\text{Cl}$ —64.5.—A colorless, ethereal liquid; boils at 11° (51.8°F.); obtained by passing gaseous HCl through ethylic alcohol to saturation, and distilling over the water-bath. It is now used to produce cold by spraying. The liquid and vapor are readily inflammable. *

By the continued action of Cl in the sunshine upon ethyl chlorid, or upon ethene chlorid, $\text{C}_2\text{H}_4\text{Cl}_2$, a white, crystalline solid, **Hexachlorethane** or **carbon trichlorid**, C_2Cl_6 , is produced. It is insoluble in H_2O , soluble in alcohol and in ether, has an aromatic odor, fuses at 160° (320°F.), and boils at 182° (359.6°F.).

Ethyl Bromid—*Hydrobromic ether*— $\text{C}_2\text{H}_5\text{Br}$ —109—A colorless, ethereal liquid; boils at 40.7° (105.3°F.) obtained by the combined action of P and Br on ethylic alcohol. It is now extensively used as an anæsthetic in minor surgery.

Ethyl Iodid—*Hydriodic ether*— $\text{C}_2\text{H}_5\text{I}$ —156—is prepared by placing absolute alcohol and P in a vessel surrounded by a freezing mixture and gradually adding I . When the action has ceased, the liquid is decanted, distilled over the water-bath and the distillate washed and rectified.

It is a colorless liquid; boils at 72.2° (162°F.); has a powerful, ethereal odor; burns with difficulty. It is largely used in the anilin industry.

[See also Esters of Glycols, p. 363.]

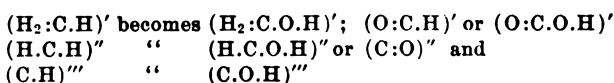
OXIDATION PRODUCTS OF THE PARAFFINS.

Many important and varied classes of compounds are derivable from the paraffins by oxidation:

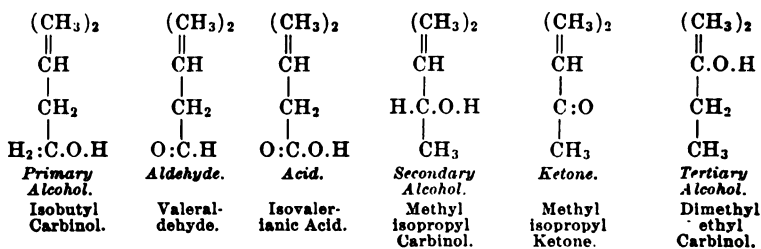
One of these may be considered as derived from the hydrocarbon by the introduction of an oxygen atom between two of its hydrocarbon groups. Thus from the hydrocarbon butane, $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_3$ we may derive the oxids $\text{CH}_3.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_3$ and $\text{CH}_3.\text{O}.\text{CH}_2.\text{CH}_2.\text{CH}_3$. These are the true oxids of the alkyls, and are known as **simple and mixed ethers**, according as the oxygen atom is symmetrically or unsymmetrically introduced. Or, in other classes of compounds, an oxygen atom may be interpolated as in the ethers, and one or more of the hydrocarbon groups may be also oxidized. In this manner compounds of very diverse nature are derived: **Esters**, such as ethyl acetate, $\text{CH}_3.\text{CO}.\text{O}.\text{CH}_2.\text{CH}_3$; **acid anhydrids**, or **acidyl oxids**, such as acetic anhydrid, $\text{CH}_3.\text{CO}.\text{O}.\text{CO}.\text{CH}_3$; certain **acids**, such as diglycollic acid, $\text{COOH}.\text{CH}_2.\text{O}.\text{CH}_2.\text{COOH}$, and certain **dihydric alcohols**, such as diethylene glycol, $\text{CH}_2\text{OH}.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_2\text{OH}$. It will be more convenient to consider these several classes of compounds after having discussed the other oxidation products.

Four other classes are more closely related to each other. They may be considered as being derived from the hydrocarbons in one of two ways; either

(1) By the interpolation or substitution, or both, of an oxygen atom or atoms in one of the groups CH_3 , CH_2 , or CH of the parent hydrocarbon (see formulæ on p. 283). Thus:

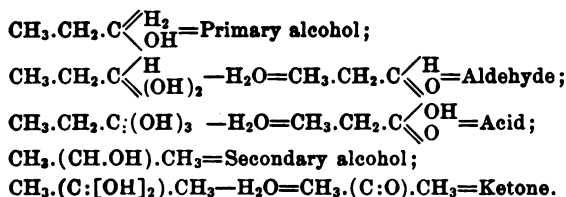


and by the oxidation of a single group in the hydrocarbon: isopentane; $(\text{CH}_3)_2:\text{CH}.\text{CH}_2.\text{CH}_3$ the following products may be obtained:

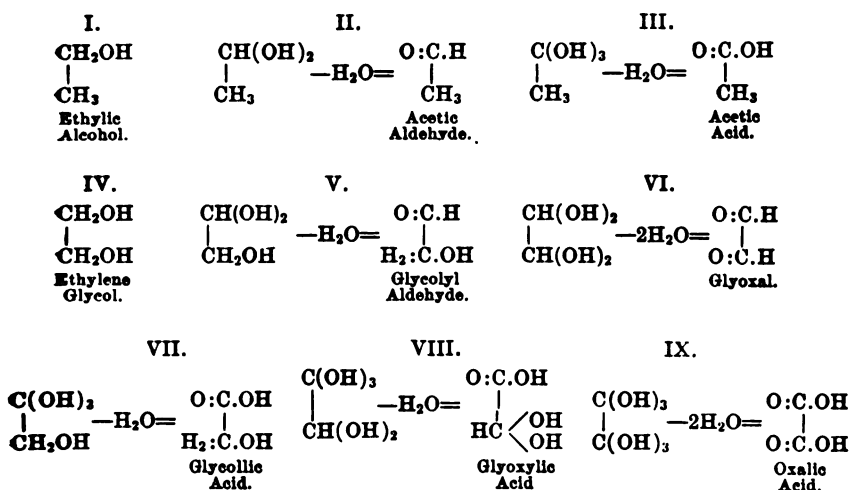


(2) Or these compounds may be considered as produced by the substitution of hydroxyls (OH), for one or more of the hydrogen atoms of the hydrocarbon, it being remembered that when a substance is thus

produced in which two hydroxyls are attached to the same carbon atom, water separates, except under the circumstances referred to on page 269. Thus from the hydrocarbon: propane, $\text{CH}_3.\text{CH}_2.\text{CH}_3$, the following products may be derived by substitution in a single hydrocarbon group :



When the number of hydroxyls substituted in each hydrocarbon group exceeds one, the number of derivatives increases rapidly with an increasing number of C atoms in the parent hydrocarbon. Thus the second term of the series, $\text{CH}_3.\text{CH}_3$, yields nine derivatives:



There are twenty-nine possible derivatives of the third hydrocarbon, $\text{CH}_3.\text{CH}_2.\text{CH}_3$.

The four classes of oxidation products under consideration are therefore :

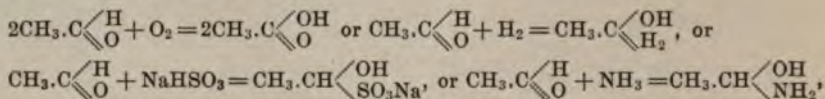
A. The alcohols, subdivided into (a) *Primary*, containing the group $-\text{C}\begin{array}{l} \nearrow \text{H}_2 \\ \searrow \text{OH} \end{array}$; (b) *Secondary*, containing the group $-\text{C}\begin{array}{l} \nearrow \text{H} \\ \searrow \text{OH} \end{array}$; and (c) *Tertiary*, containing the group $\equiv \text{C}.\text{OH}$;

B. The aldehydes, containing the group $-\text{C}\begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array}$;

C. The ketones, containing the group $=\text{C}=\text{O}$; and

D. The carboxylic acids, containing the group carboxyl: $-\text{C}\begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$.

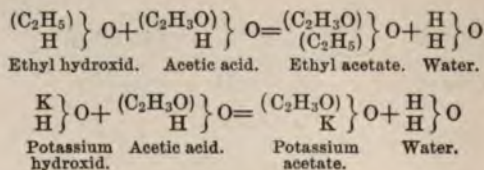
The aldehydes and ketones of this series contain no double linkages between carbon atoms, and, in that sense, are saturated compounds, but they form products of addition, and in that sense are unsaturated (p. 269). Thus



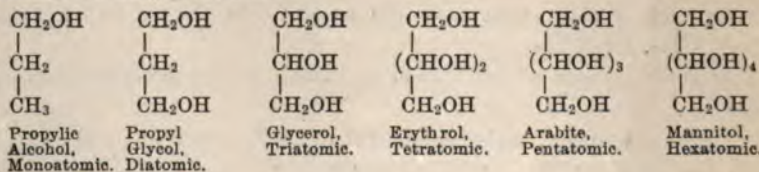
and $\text{CH}_3.\text{CO}.\text{CH}_3 + \text{H}_2 = \text{CH}_3.\text{CHOH}.\text{CH}_3$. But it is not to be inferred from the presence of a $\text{C}=\text{O}$ group in a molecule that the substance can form products of addition by the breaking out of the double linkage between C and O, as in some of the above reactions. Many compounds containing CO, such as the carboxylic acids, containing $(\text{O}:\text{C}.\text{OH})'$ do not do so.

ALCOHOLS—HYDROCARBON HYDROXIDS.

These substances are mainly characterized by their power of entering into double decomposition with acids to form neutral compounds, called **esters**, water being at the same time formed at the expense of both alcohol and acid. They are the hydroxids of hydrocarbon radicals, the alkyls, and as such resemble the metallic hydroxids, while the esters are the counterparts of the metallic salts:



Or they may be regarded as substances derived from the hydrocarbons by the substitution of one or more hydroxyls for one or more hydrogen atoms. Alcohols containing one OH are designated as **monoatomic** or **monohydric**; those containing two OH groups are **diatomic** or **dihydric**, etc.:



MONOATOMIC, OR MONOHYDRIC ALCOHOLS.

Beginning with the third member of the series, an increasing number of isomeres of the higher terms are known.

I. Some of these alcohols yield on oxidation, first, an aldehyde containing the group (CHO)' and then an acid containing the group (COOH)', both aldehyde and acid containing the same number of carbon atoms as the alcohol. These alcohols contain the characterizing group (CH₂OH)', and are called **primary alcohols**, e. g., ethylic alcohol: CH₃.CH₂OH.

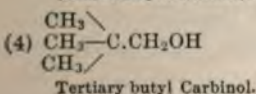
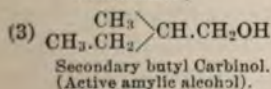
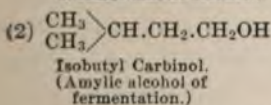
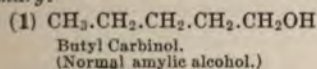
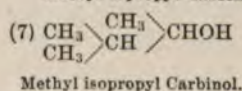
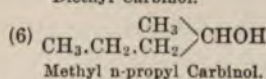
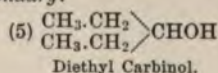
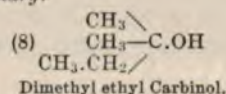
II. Other monoatomic alcohols yield on oxidation, not an aldehyde or an acid, but a ketone, containing the group (CO)'' and the same number of carbon atoms as the alcohol. These alcohols contain the characterizing group (CHOH)'', and are called **secondary alcohols**, or **isoalcohols**, e. g., Isopropyl alcohol: CH₃.CHOH.CH₃.

III. Still other alcohols yield on oxidation either two or more acids, or an acid and a ketone, whose molecules contain a less number of carbon atoms than the alcohol from which they were derived. These alcohols contain the characterizing group (COH)''', and are called **tertiary alcohols**, e. g., Tertiary butyl alcohol, (CH₃)₃.COH.

The monohydric alcohols are also the hydroxids of the *alkyls* (p. 274).

Nomenclature.—Names of alcohols terminate in *ol*; and the termination *ol* is reserved for the names of alcohols and of phenols. The "Geneva" names of the monohydric alcohols are derived from those of the corresponding hydrocarbons by the substitution of the syllable *ol* for the terminal *e*: Thus H.CH₂OH is Methanol; CH₃.CH₂.OH ethanol; CH₃.CH₂.CH₂OH, 1-propanol; CH₃.CHOH.CH₃, 2-propanol, etc.

Kolbe's system of naming the monoatomic alcohols is more generally followed. It refers the names of the higher alcohols back to that of the first, H.CH₂OH, which is called **carbinol**; the names of the radicals contained in the superior homologues being prefixed to the word "*carbinol*" in the construction of their names. Thus the graphic formulæ and **carbinol names** of the eight possible amylic alcohols are as follows:

Primary.*Secondary.**Tertiary.*

Of the above, numbers 1, 5 and 6 are derived from the normal paraffin (1, page 274); numbers 2, 3, 7 and 8 from the isoparaffin (2), and number 4 from the mesoparaffin (3).

Primary, secondary and tertiary alcohols of this series, containing less than nine carbon atoms, may be distinguished from each other by conversion into nitrolic acids (p. 376). The three classes of alcohols also differ in the facility with which they yield esters (p. 358) with organic acids. Primary alcohols are rapidly esterified in large amount, secondary alcohols in less proportion, and more slowly; tertiary alcohols very slowly and to a maximum amount of about 7 per cent.

General Methods of Formation.—(1) By the action of freshly precipitated, moist silver hydroxid upon the haloid esters: $\text{C}_2\text{H}_5\text{I} + \text{AgHO} = \text{C}_2\text{H}_5\text{OH} + \text{AgI}$.

(2) By the saponification of their esters by caustic potash: $\text{C}_2\text{H}_3\text{O}_2.\text{C}_2\text{H}_5 + \text{KHO} = \text{C}_2\text{H}_5.\text{OH} + \text{C}_2\text{H}_3\text{O}_2\text{K}$.

(3) Primary alcohols are produced by the reduction of aldehydes, acid chlorids, or anhydrids (pp. 299, 352, 351): $\text{C}_2\text{H}_5.\text{CHO} + \text{H}_2 = \text{C}_2\text{H}_5.\text{CH}_2\text{OH}$, or $\text{C}_2\text{H}_5.\text{COCl} + 2\text{H}_2 = \text{C}_2\text{H}_5.\text{CH}_2\text{OH} + \text{HCl}$, or $(\text{CH}_3.\text{CO})_2\text{O} + 2\text{H}_2 = \text{CH}_3.\text{CH}_2\text{OH} + \text{CH}_3.\text{COOH}$.

(4) By the action of nitrous acid upon the primary amins (p. 379): $\text{CH}_3.\text{CH}_2.\text{NH}_2 + \text{HNO}_2 = \text{CH}_3.\text{CH}_2\text{OH} + \text{N}_2 + \text{H}_2\text{O}$.

(5) Secondary alcohols are formed by the reduction of ketones: $\text{CH}_3.\text{CO}.\text{CH}_3 + \text{H}_2 = \text{CH}_3.\text{CHOH}.\text{CH}_3$.

General Reactions.—(1) The monohydric alcohols react with metallic Na or K to form double oxids, called **alcoholates**: $2\text{CH}_3.\text{CH}_2.\text{OH} + \text{Na}_2 = \text{H}_2\text{O} + 2\text{CH}_3.\text{CH}_2.\text{O}.\text{Na}$.

(2) When heated with acids they form esters (p. 358): $\text{CH}_3.\text{CH}_2.\text{OH} + \text{H}_2\text{SO}_4 = \text{CH}_3.\text{CH}_2.\text{HSO}_4 + \text{H}_2\text{O}$, or $2\text{CH}_3.\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4 = (\text{CH}_3.\text{CH}_2)_2\text{SO}_4 + 2\text{H}_2\text{O}$.

(3) When heated with hydracids they form alkyl halids: $\text{CH}_3.\text{CH}_2.\text{OH} + \text{HCl} = \text{CH}_3.\text{CH}_2\text{Cl} + \text{H}_2\text{O}$; which, in turn, when reduced by nascent hydrogen, regenerate the parent hydrocarbon: $\text{CH}_3\text{CH}_2\text{Cl} + \text{H}_2 = \text{CH}_3.\text{CH}_3 + \text{HCl}$.

(4) Their products of oxidation vary according as they are primary, secondary or tertiary (see above): *Primary*: $2\text{CH}_3.\text{CH}_2\text{OH} + \text{O}_2 = 2\text{CH}_3.\text{CHO} + 2\text{H}_2\text{O}$, and $\text{CH}_3.\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_3.\text{COOH} + \text{H}_2\text{O}$; *Secondary*: $2\text{CH}_3.\text{CHOH}.\text{CH}_3 + \text{O}_2 = 2\text{CH}_3.\text{CO}.\text{CH}_3 + 2\text{H}_2\text{O}$; *Tertiary*: $2(\text{CH}_3)_3.\text{COH} + 3\text{O}_2 = 2\text{CH}_3.\text{CO}.\text{CH}_3 + 2\text{H}.\text{COOH} + 2\text{H}_2\text{O}$, then $\text{CH}_3.\text{CO}.\text{CH}_3 = 2\text{O}_2 = \text{CH}_3.\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$, and $2\text{H}.\text{COOH} + \text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$.

Methyl Hydroxid—Carbinol—Pyroxylic spirit—Methylic alcohol—Wood spirit— $\text{H}.\text{CH}_2\text{OH} = 32$ —may be formed from marsh-gas, CH_3H , by first converting it into the iodid, and acting upon this with potassium hydroxid: $\text{CH}_3\text{I} + \text{KHO} = \text{KI} + \text{H}.\text{CH}_2\text{OH}$. It is usually obtained by the destructive distillation of wood. The pure hydroxid can

only be obtained by decomposing a crystalline compound, such as methyl oxalate, and rectifying the product until the boiling-point is constant at 66.5° (151.7° F.). Pure methyl alcohol is a colorless liquid, having an ethereal and alcoholic odor, and a sharp, burning taste; sp. gr. 0.814 at 0° ; boils at 66.5° (151.7° F.); burns with a pale flame, giving less heat than that of ethylic alcohol; mixes with water, alcohol, and ether in all proportions; is a good solvent of resinous substances, and also dissolves sulfur, phosphorus, potash, and soda.

Methyl hydroxid is not affected by exposure to air under ordinary circumstances, but in the presence of platinum-black it is oxidized, with formation of the corresponding aldehyde, formaldehyde, and acid, formic acid. Hot HNO_3 decomposes it with formation of nitrous fumes, formic acid and methyl nitrate. It is acted upon by H_2SO_4 in the same way as ethyl alcohol. The organic acids form methyl esters with it.

Methylated spirit is ethyl alcohol containing one-ninth its volume of wood spirit.

Ethyl Hydroxid—Ethylic alcohol—Methyl carbinol—Vinic alcohol—Alcohol—Spirits of wine— $\text{CH}_3.\text{CH}_2\text{OH}$ —46.

Preparation.—Industrially alcohol and alcoholic liquids are obtained from substances rich in starch or glucose.

The manufacture of alcohol consists of three distinct processes: (1) the conversion of starch into sugar; (2) the fermentation of the saccharine liquid; (3) the separation, by distillation, of the alcohol formed by fermentation.

The raw materials for the first process are **malt** and some substance (grain, potatoes, rice, corn, etc.) containing starch. Malt is barley which has been allowed to germinate, and, at the proper stage of germination, roasted. During this growth there is developed in the barley a peculiar nitrogenous principle called **diastase** (p. 605). The starchy material is mixed with a suitable quantity of malt and water, and the mass maintained at a temperature of 65° – 70° (149° – 158° F.) for two to three hours, during which the diastase rapidly converts the starch into **dextrin**, and this in turn into **maltose** and **glucose** (p. 322).

The saccharine fluid, or **wort**, obtained in the first process, is drawn off, cooled, and **yeast** is added. As a result of the growth of the yeast-plant, a complicated series of chemical changes take place, the principal one of which is the splitting up of the glucose into carbon dioxid and alcohol: $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$. There are formed at the same time small quantities of glycerol, succinic acid, and propylic, butylic, and amylic alcohols (p. 600).

An aqueous fluid is thus obtained which contains 3–15 per cent of alcohol. This is then separated by the third process, that of distillation and rectification. The apparatus used for this purpose has

been so far perfected that by a single distillation an alcohol of 90-95 per cent can be obtained.

In some cases alcohol is prepared from fluids rich in glucose, such as grape-juice, molasses, syrup, etc. In such cases the first process becomes unnecessary.

Commercial alcohol always contains H_2O , and when pure or *absolute* alcohol is required, the commercial product must be mixed with some hygroscopic solid substance, such as quicklime, from which it is distilled after having remained in contact twenty-four hours.

An interesting total synthesis of alcohol is from calcium carbide, water and hydrogen. Acetylene is formed by the action of water upon calcium carbide, $CaC_2 + 2H_2O = CaH_2O_2 + C_2H_2$; vapors of acetylene and water, heated together to 325° (617° F.) unite to form aldehyde, $C_2H_2 + H_2O = CHO.CH_3$; and nascent hydrogen converts aldehyde into alcohol, $CHO.CH_3 + H_2 = CH_2OH.CH_3$.

Properties.—Alcohol is a thin, colorless, transparent liquid, having a spirituous odor and a sharp, burning taste; sp. gr. 0.8095 at 0° , 0.7939 at 15° (59° F.); it boils at 78.5° (173.3° F.), and solidifies at -130.5° (-202.9° F.). At temperatures below -90° (-130° F.) it is viscous. It mixes with water in all proportions, the union being attended by elevation in temperature and contraction in volume (after cooling to the original temperature). It also attracts moisture from the air to such a degree that absolute alcohol only remains such for a very short time after its preparation. It is to this power of attracting H_2O that alcohol owes its preservative power for animal substances. It is a very useful solvent, dissolving a number of gases, many mineral and organic acids and alkalies, most of the chlorids and carbonates, some of the nitrates, and the essences and resins. The sulfates are insoluble in alcohol. Alcoholic solutions of fixed medicinal substances are called **tinctures**; those of volatile principles, **spirits**.

The action of oxygen upon alcohol varies according to the conditions. Under the influence of energetic oxidants, such as chromic acid, or, when alcohol is burned in the air, the oxidation is rapid and complete, and is attended by the extrication of much heat, and the formation of carbon dioxid and water: $C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$. Mixtures of air and vapor of alcohol explode upon contact with flame. If a less active oxidant be used, such as platinum-black, or by the action of atmospheric oxygen at low temperatures, a simple oxidation of the alcoholic radical takes place, with formation of *acetic acid*: $CH_3.CH_2OH + O_2 = CH_3.COOH + H_2O$, a reaction which is utilized in the manufacture of acetic acid and vinegar. If the oxidation be still further limited, *aldehyde* is formed: $2CH_3.CH_2OH +$

$O_2=2CH_3.CHO+2H_2O$. If vapor of alcohol be passed through a tube filled with platinum sponge and heated to redness, or if a coil of heated platinum wire be introduced into an atmosphere of alcohol vapor, the products of oxidation are quite numerous: among them are water, ethylene, aldehyde, acetylene, carbon monoxid, and acetal. Heated platinum wire introduced into vapor of alcohol continues to glow by the heat resulting from the oxidation, a fact which has been utilized in the thermocautery.

Chlorin and bromin act energetically upon alcohol, producing a number of chlorinated and brominated derivatives, the final products being *chloral* and *bromal* (p. 307). If the action of Cl be moderated, aldehyde and HCl are first produced. Iodin acts quite slowly in the cold, but old solutions of I in alcohol (Tr. iodin.) are found to contain HI, ethyl iodid, and other imperfectly studied products. In the presence of an alkali, I acts upon alcohol to produce iodoform. Potassium and sodium dissolve in alcohol with evolution of H; upon cooling, a white solid crystallizes, which is the double oxid of ethyl and the alkali metal, and is known as potassium or sodium **ethylate** or **alcoholate**. Nitric acid, aided by a gentle heat, acts violently upon alcohol, producing nitrous ether, brown fumes, and products of oxidation. (For the action of other acids upon alcohol see the corresponding esters and the ethers.) The hydroxids of the alkali metals dissolve in alcohol, but react upon it slowly; the solution turns brown and contains an acetate. If alcohol be gently heated with HNO_3 and nitrate of silver or of mercury, a gray precipitate falls, which is silver or mercury fulminate.

Varieties.—It occurs in different degrees of concentration: **absolute alcohol** is pure alcohol, C_2H_6O . It is not purchasable, and must be made as required. The so-called absolute alcohol of the shops is rarely stronger than 98 per cent. **Alcohol** (U. S.), sp. gr. 0.820, contains 94 per cent. by volume, and **spiritus rectificatus** (Br.), sp. gr. 0.838, contains 84 per cent. This is the ordinary rectified spirit used in the arts. **Alcohol dilutum** (U. S.)=**Spiritus tenuior** (Br.), sp. gr. 0.920, used in the preparation of tinctures, contains 53 per cent. It is of about the same strength as the **proof spirit** of commerce.

Analytical Characters.—(1) Heated with a small quantity of solution of potassium dichromate and H_2SO_4 , the liquid assumes an emerald-green color, and, if the quantity of C_2H_6O be not very small, the peculiar fruity odor of aldehyde is developed. (2) Warmed and treated with a few drops of potash solution and a small quantity of iodine, an alcoholic liquid deposits a yellow, crystalline ppt. of iodoform, either immediately or after a time. (3) If HNO_3 be added to a liquid containing C_2H_6O , nitrous ether, recognizable by its odor, is given off. If a solution of mercurous nitrate with excess of HNO_3

be then added, and the mixture heated, a further evolution of nitrous ether occurs, and a yellow-gray deposit of fulminating mercury is formed, which may be collected, washed, dried, and exploded. (4) If an alcoholic liquid be heated for a few moments with H_2SO_4 diluted with H_2O and distilled, the distillate, on treatment with H_2SO_4 and potassium permanganate, and afterward with sodium thiosulfate, yields aldehyde, which may be recognized by the production of a violet color with a dilute solution of fuchsin.

None of the above reactions, *taken singly*, is characteristic of alcohol.

Alcohol is determined quantitatively in simple mixtures of alcohol and water by determining the specific gravity and referring to tables constructed for the purpose. In alcoholic beverages 100 cc. of the sample is distilled until 75 cc. have passed over, the distillate is then made up to 100 cc. with water, and the sp. gr. determined.

Alcoholic Beverages.—These may be divided into four classes:

I.—Those prepared by the fermentation of malted grain—**beers, ales and porters.**

II.—Those prepared by the fermentation of grape juice—**wines.**

III.—Those prepared by the fermentation of the juices of fruits other than the grape—**cider, fruit-wines.**

IV.—Those prepared by the distillation of some fermented saccharine liquid—**ardent spirits.**

Beer, ale and porter are aqueous infusions or decoctions of malted grain, fermented and flavored with hops. They contain all of the soluble constituents of the grain and hops, plus dextrins, maltose, glucose, alcohol and carbon dioxid. Their alcoholic content varies from 1.5 to 9 per cent absolute alcohol by weight. They contain a considerable proportion of nitrogenous material (0.4 to 1 per cent N), and succinic, lactic and acetic acids. The most serious adulterations of malt liquors consist in the use of artificial glucose to furnish a part of the alcohol, and in the use of strychnin, picrotoxin, picric acid, or other bitter principles as substitutes for hops.

Wine is fermented grape-juice. The expressed juice, called the **must**, contains much glucose, the fermentation of which is set up by yeast-plants growing upon the grape-skins. In red wines the color is produced by solution of the coloring matter of the skins in the accumulating alcohol. The same agency causes the precipitation of a part of the hydropotassic tartrate, to which the grape or wine owes its tartness. Sweet wines are made from grapes rich in glucose, and by arresting the fermentation before the sugar has been completely decomposed. "Dry" or "brut" wines, which are not sweet, are fermented to completion. "Light" wines are such as contain less than 12 per cent of alcohol, although they sometimes contain as much as 16 per cent.

They are the products of temperate climates, and include the clarets, Sauternes, Burgundies, the Rhine, Moselle, Australian, Greek and Hungarian wines, and the wines of the northern portions of Spain, Italy and the United States. The champagnes also belong to this class, and are sparkling from the escape of carbon dioxide, produced by a secondary fermentation in the bottles, and held in solution by its own pressure. "Heavy" wines are those whose alcoholic strength is greater than 12 per cent, usually 14 to 25 per cent. They are the products of warm climates, and include the sherries of the south of Spain, the ports of Portugal, the Marsalas of the south of Italy, the Madeiras, and the wines of southern California. The adulteration of real wine is practically limited to the addition of coloring matters, and to "fortification" by the addition of alcohol or brandy. Liquids are also manufactured to imitate wines, which contain no grape-juice.

Cider is the fermented juice of the apple, and contains from 3.5 to 7.5 per cent of alcohol.

Spirits are prepared by fermentation and distillation. They differ from beers and wines in containing a larger percentage of alcohol, 35 to 50 per cent, and in not containing any of the non-volatile constituents of the grains or fruits from which they are prepared. They are yellow in color when stored in white oak casks the interior of which has been burnt, and colorless or faintly yellow when kept in unburnt casks. Besides alcohol and water they contain acetic, butyric, valeric and cænanthic esters, to which they owe their flavor. They include: brandy, sp. gr. 0.929–0.934, made by distilling wine; rum, sp. gr. 0.914–0.926, made by distilling molasses; and whiskies and gins, made by fermenting and distilling grains, wheat, rye, barley or maize. The peculiar flavor of Scotch and Irish whiskies is derived from the smoke of a peat fire; that of gin is produced by distilling from juniper berries. In making "straight" whisky the distillate is not completely defuselated (p. 292), and by slow oxidation the remaining fusel produces the esters to which the spirit owes its flavor. Hence when newly made it is neither palatable nor wholesome, but in about three years in wood the fusel has been in great part removed by oxidation, the whisky is "ripe," and continues to improve with age. In making "blend" whisky the distillate is completely defuselated to "neutral spirit," and the product is made to imitate aged whisky more or less closely by addition of esters, "beading oil" and other chemicals.

Propyl Hydroxid—Ethyl carbinol—Primary propyl alcohol— $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ —60—is produced, along with ethylic alcohol, during fermentation, and obtained by fractional distillation of marc brandy, from *cognac pil*, *huile de marc* (not to be confounded with oil of wine), an oily matter, possessing the flavor of inferior brandy, which separates from marc brandy, distilled at high temperatures;

and from the residues of manufacture of alcohol from beet-root, grain, molasses, etc. It is a colorless liquid, has a hot alcoholic taste, and a fruity odor; boils at 96.7° (206.1° F.); and is miscible with water. It has not been put to any use in the arts. Its intoxicating and poisonous actions are greater than those of ethyl alcohol. It exists in small quantity in cider.

Butyl Alcohols— C_4H_9OH —74.—The four butyl alcohols theoretically possible are known to exist:

Propyl Carbinol—Primary normal butyl alcohol—*Butyl alcohol of fermentation*— $CH_3.CH_2.CH_2.CH_2OH$ —is formed in small quantities during alcoholic fermentation, and may be obtained by repeated fractional distillation from the oily liquid left in the rectification of vinic alcohol. It is a colorless liquid; boils at 116.8° (245.8° F.). It is more actively poisonous than ethyl or methyl alcohol.

Isopropyl Carbinol—Isobutyl alcohol— $\begin{smallmatrix} CH_3 \\ | \\ CH_3 \end{smallmatrix} > CH.CH_2OH$ —occurs in the fusel oil obtained in the products of fermentation and distillation of beet-root molasses. It is a colorless liquid, sp. gr. 0.8032; boils at 108.4° (219.1° F.).

Ethyl-methyl Carbinol—Secondary butyl alcohol—*Butylene hydrate*— $\begin{smallmatrix} CH_3-CH_2 \\ | \\ CH_3 \end{smallmatrix} > CHOH$ —a liquid which boils at 99° (210.2° F.).

Trimethyl Carbinol—Tertiary butyl alcohol, $\begin{smallmatrix} CH_3 \\ | \\ CH_3-CH_2 \\ | \\ CH_3 \end{smallmatrix} > COH$ —a crystalline solid which fuses at 25° (77° F.), and boils at 82° (179.6° F.).

Amylic Alcohols— $C_5H_{11}OH$ —88.—The eight amyl alcohols theoretically possible (see p. 285) are known. The substance usually known as **amylic alcohol**, **potato spirit**, **fusel oil**, **alcohol amylicum** (Br.), is the primary alcohol, $\begin{smallmatrix} CH_3 \\ | \\ CH_3 \end{smallmatrix} > CH.CH_2.CH_2OH$, with lesser quantities of other alcohols, differing in nature and amount with the grain used, and the conditions of the fermentation and distillation, each kind of "spirit" furnishing and containing a peculiar fusel.

In the process of manufacture of ardent spirits the fusel oil accumulates in great part in the still, but much of it distils over, and is more or less completely removed from the product by the process of defuselation.

Spirits properly freed of fusel oil give off no irritating or foul fumes when hot. They are not colored red when mixed with three parts C_2H_6O and one part strong H_2SO_4 . They are not colored red or black by ammoniacal silver nitrate solution. When 150 parts of the spirit, mixed with 1 part potash, dissolved in a little H_2O , are evaporated down to 15 parts, and mixed with an equal volume of dilute H_2SO_4 , no offensive odor should be given off.

While young spirits owe their rough taste, and, in great measure, their intoxicating qualities to the presence of fusel oil, it is a popula-

error that a whisky would be improved by complete removal of all products except ethyl alcohol. The improvement of a spirit by age is due to chemical changes in the small amount of fusel retained in a properly manufactured product, and, were this absent, the spirit would deteriorate rather than improve by age.

The individual amylic alcohols have the following characters: **Butyl carbinol**; normal amylic alcohol, $\text{—CH}_3\text{.CH}_2\text{.CH}_2\text{.CH}_2\text{.CH}_2\text{OH}$ —is a colorless liquid, boils at 137° (278.6° F.). Obtained from normal butyl alcohol, or from normal amylamin. It yields normal valerianic acid on oxidation.

Isobutyl Carbinol—Amyl alcohol— $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ —is the principal constituent of the fusel oil from grain and potatoes. It is obtained from the last milky products of rectification of alcoholic liquids. These are shaken with H_2O to remove ethyl alcohol, the supernatant oily fluid is decanted, dried by contact with fused calcium chlorid, and distilled; that portion which passes over between 128° and 132° (262.4° – 269.6° F.) being collected.

It is a colorless, oily liquid, has an acrid taste and a peculiar odor, at first not unpleasant, afterward nauseating and provocative of severe headache. It boils at 131.4° (236.5° F.), and crystallizes at -20° (4° F.); sp. gr. 0.8184 at 15° (5° F.). It mixes with alcohol and ether, but not with water. It burns with a pale blue flame when sufficiently heated.

When exposed to air it oxidizes very slowly; quite rapidly, however, in contact with platinum-black, forming isovalerianic acid. The same acid, along with other substances, is produced by the action of the more powerful oxidants upon amyl alcohol. Chlorin attacks it energetically, forming amyl chlorid, HCl , and other chlorinated derivatives. Sulfuric acid dissolves in amyl alcohol, with formation of amyl-sulfuric acid, $\text{SO}_4(\text{C}_5\text{H}_{11})\text{H}$, corresponding to ethyl-sulfuric acid (p. 359). It also forms similar acids with phosphoric, oxalic, citric, and tartaric acids. Its esters, when dissolved in ethyl alcohol, have the taste and odor of various fruits, and are used in the preparation of artificial fruit-essences. Amyl alcohol is also used in analysis as a solvent, particularly for certain alkaloids, and in pharmacy for the artificial production of valerianic acid and the valerianates.

Diethyl Carbinol— $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ —is produced by the action of a mixture of zinc and ethyl iodid on ethyl formate, with the subsequent addition of H_2O . It is a liquid which boils at 116.5° (241.7° F.).

Methyl-propyl Carbinol— $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$ —a liquid, boiling at 118.5° (245.3° F.), obtained by the hydrogenation of methyl-propylic acetone.

Methyl-isopropyl Carbinol— $(\text{CH}_3)_2=\overset{\text{CH}_3}{\text{CH}}\text{>CHOH}$ —obtained by the hydrogenation of methyl-isopropyl acetone; or by the action of hydriodic acid upon amylene, and the action of moist silver oxid upon the product so obtained. It is a colorless liquid, sp. gr. 0.829 at 0° (32° F.), having a pungent, ethereal odor; boils at 112.5° (234.5° F.), soluble in H_2O and in alcohol.

Ethyl-dimethyl Carbinol—*Tertiary amylic alcohol*—*Amylene hydrate*— $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}_2}}\text{COH}$ —is a liquid which solidifies at -12° (10.4° F.) and boils at 102.5° (216.5° F.); formed by the action of zinc methyl upon propionyl chlorid, or by decomposition of tertiary sulfamylic acid by boiling H_2O . The nitrite of this alcohol has been used as a substitute for amyl nitrite.

Cetyl Hydroxid—*Cetylic alcohol*—*Ethal*— $\text{C}_{16}\text{H}_{33}\text{OH}$ —242—is obtained by the saponification of spermaceti (its palmitic ester). It is a white, crystalline solid; fusible at 49° (120.2° F.); insoluble in H_2O ; soluble in alcohol and ether; tasteless and odorless.

Ceryl Hydroxid— $\text{C}_{27}\text{H}_{55}\text{OH}$ —396—and **Miricyl Hydroxid**— $\text{C}_{30}\text{H}_{61}\text{OH}$ —438—are obtained as white crystalline solids; the former from China wax; the latter from beeswax, by saponification.

DIATOMIC, OR DIHYDRIC ALCOHOLS; GLYCOLS.

The paraffin glycols are derived from the paraffins by the substitution of two hydroxyls for two H atoms. They bear the same relation to the monoatomic alcohols that the diacid bases bear to the monacid bases. They are diprimary, dissecondary, primary-secondary, etc., according as they contain groups CH_2OH ; CHOH , or COH . Their "Geneva" names are derived from those of the parent hydrocarbons by the substitution of the syllable "*diol*" for the terminal *e*; and they are distinguished as α , β , γ , δ , etc., according as the hydroxyls occupy 1:2, 1:3, 1:4, 1:5, etc., positions. Thus the primary-secondary glycol $\text{CH}_2\text{OH}.\text{CH}_2.\text{CHOH}.\text{CH}_3$, is β -butandiol (p. 340).

As the monohydric alcohols are regarded as the hydroxids of the univalent *alkyls* (p. 284), so the dihydric alcohols are considered as the hydroxids of bivalent hydrocarbon radicals: $(\text{C}_2\text{H}_4)''$: $(\text{OH})_2$, which are called **alkylens**.

They may be obtained from the neutral haloid esters by heating with silver acetate: $\text{C}_2\text{H}_4\text{I}_2 + 2\text{AgC}_2\text{H}_3\text{O}_2 = 2\text{AgI} + \text{C}_2\text{H}_4(\text{C}_2\text{H}_3\text{O}_2)_2$, and saponification of the ester so formed by caustic potash: $\text{C}_2\text{H}_4(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{KHO} = \text{C}_2\text{H}_4(\text{OH})_2 + 2\text{KC}_2\text{H}_3\text{O}_2$ (see p. 363).

While the monoatomic alcohols are only capable of forming a single ester with a monobasic acid, the glycols are capable of forming two such esters: CH_2OH , $\text{CH}_2(\text{C}_2\text{H}_3\text{O}_2)'$ and C_2H_4 : $(\text{C}_2\text{H}_3\text{O}_2)_2$.

Methene Glycol, which would have the composition $\text{H}_2\text{C} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{OH} \end{smallmatrix}$, is not known (p. 269). Its haloid esters are, however, known. A condensation product corresponding to it exists as **methene dimethylate**, $\text{H}_2\text{C} \begin{smallmatrix} \diagup \text{OCH}_3 \\ \diagdown \text{OCH}_3 \end{smallmatrix}$, also called **methylal** and **formal**, as a thin liquid, boiling at 42° (107.6°F.), soluble in alcohol, ether, and water, sp. gr. 0.855; formed by oxidizing methyl alcohol with H_2SO_4 and MnO_2 . It has been used as a medicine.

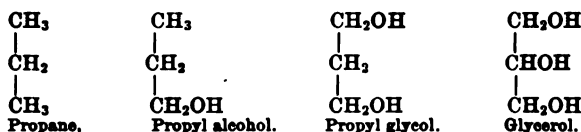
Ethene Glycol—**Ethylene glycol**, or alcohol, or hydroxid— $\begin{smallmatrix} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{smallmatrix}$ —62.—This, the best known of the glycols, is prepared by the action of dry silver acetate upon ethylene bromid. The ester so obtained is purified by redistillation, and decomposed by heating for some time with barium hydroxid.

It is a colorless, slightly viscous liquid; odorless; faintly sweet; sp. gr. 1.125 at 0° (32°F.); boils at 197° (386.6°F.); sparingly soluble in ether; very soluble in water and in alcohol.

It is not oxidized by simple exposure to air, but on contact with platinum-black it is oxidized to glycolic acid; more energetic oxidants transform it into oxalic acid. Chlorin acts slowly upon glycol in the cold; more rapidly under the influence of heat, producing chlorinated and other derivatives. By the action of dry HCl upon cooled glycol, a product is formed, intermediate between it and ethylene chlorid, a neutral compound—**ethene chlorhydrin**, $\begin{smallmatrix} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{Cl} \end{smallmatrix}$, which boils at 130° (266°F.).

TRIAOMIC, OR TRIHYDRIC ALCOHOLS; GLYCEROLS.

These are derived from the paraffins by the substitution of three hydroxyls for three hydrogen atoms, linked to different carbon atoms. The simplest triprimary glycerol, which would have the formula: $\text{CH}(\text{CH}_2\text{OH})_3$, is unknown. The simplest known representative of the class is the ordinary glycerine, more properly called **glycerol**, which is diprimary-secondary. The relations of the monoatomic, diatomic, and triatomic alcohols to each other and to the parent hydrocarbon are shown in the following formulæ:



The Geneva names of the glycerols are derived from those of the hydrocarbons by the substitution of the syllable "*triol*" for the terminal *e*. Thus glycerol is **propantriol**.

They are obtained by the saponification of their esters, either those existing in nature or those produced artificially.

They combine with acids to form three series of esters, known generically as **monoglycerids**, **diglycerids**, and **triglycerids**, formed by the combination of one molecule of the alcohol with one, two, or three molecules of a monobasic acid. The names of the individual esters terminate in *in*, and have a prefix indicating the number of acid residues. Thus: $\text{C}_3\text{H}_5(\text{OH})_2.\text{C}_2\text{H}_3\text{O}_2$ is **monacetin**, $\text{C}_3\text{H}_5(\text{OH})(\text{C}_2\text{H}_3\text{O}_2)_2$ is **diacetin**, and $\text{C}_3\text{H}_5(\text{C}_2\text{H}_3\text{O}_2)_3$ is **triacetin** (p. 364).

Glycerol—Glycerin—Propenyl alcohol—Glycerinum (U. S.)— $\text{C}_3\text{H}_5(\text{OH})_3$ —92—was first obtained as a secondary product in the manufacture of lead plaster; it is now produced as a by-product in the manufacture of soaps and of stearin candles. It exists free in palm-oil and in other vegetable oils. It is produced in small quantity during alcoholic fermentation, and is consequently present in wine and beer. It is much more widely disseminated in its esters, the neutral fats, in the animal and vegetable kingdoms.

It has been obtained by partial synthesis, by heating a mixture of allyl tribromid, silver acetate and acetic acid, and saponifying the triacetin so obtained. Also by total synthesis, by reduction of dioxycetone (p. 310) by sodium amalgam in presence of aluminium sulfate: $\text{CH}_2\text{OH}.\text{CO}.\text{CH}_2\text{OH} + \text{H}_2 = \text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$.

Glycerol obtained by saponification of fats, and purified by distillation in a current of superheated steam, known as "distilled glycerin," is reasonably pure. The only impurities likely to be present are water, and sometimes arsenic.

Glycerol is a colorless, odorless, syrupy liquid, has a sweetish taste; sp. gr. 1.26 at 15° (59°F.). Although it cannot usually be caused to crystallize by the application of the most intense cold, it does so sometimes under imperfectly understood conditions, forming small, white needles of sp. gr. 1.268, and fusible between 17° and 18° (62.6° and 64.6°F.). It is soluble in all proportions in water and alcohol, insoluble in ether and in chloroform. It is a good solvent for a number of mineral and organic substances (*glycerites* and *glyceroles*). It is not volatile at ordinary temperatures. When impure glycerol is heated, a portion distils unaltered at 275° – 280° (527° – 536°F.), but the greater part is decomposed into acrolein, acetic acid, carbon dioxid, and combustible gases. It may be distilled unchanged in a current of superheated steam between 285° and 315° (545° – 599°F.). Pure glycerol distils unchanged at 290° at a pressure of 756 mm., and at 180° at 20 mm.

Concentrated glycerol, when heated to 150° (302°F.) ignites and burns without odor and without leaving a residue, and with a pale blue flame. It may also be burnt from a short wick.

Glycerol is readily oxidized, yielding different products with different degrees of oxidation. Platinum-black oxidizes it, with formation, finally, of H_2O and CO_2 . Oxidized by manganese dioxid and H_2SO_4 , it yields CO_2 and formic acid. If a layer of glycerol diluted with an equal volume of H_2O be floated on the surface of HNO_3 of sp. gr. 1.5, a mixture of several acids is formed: oxalic, $\text{C}_2\text{O}_4\text{H}_2$; glyceric, $\text{C}_3\text{H}_6\text{O}_4$, formic, CH_2O_2 ; glycollic, $\text{C}_2\text{H}_4\text{O}_3$; glyoxylic, $\text{C}_2\text{H}_4\text{O}_4$; and tartaric, $\text{C}_4\text{H}_6\text{O}_6$. When glycerol is heated with potassium hydroxid, a mixture of potassium acetate and formate is produced. When glycerol, diluted with 20 volumes of H_2O , is heated with Br ; CO_2 , bromoform, glyceric acid, and HBr are produced. Phosphoric anhydrid removes the elements of H_2O from glycerol, with formation of acrolein (p. 427). A similar action is effected by heating with H_2SO_4 , or with monopotassic sulfate. Heated with oxalic acid, glycerol yields CO_2 and formic acid.

The presence of glycerol in a liquid may be detected as follows: Add NaHO to feebly alkaline reaction, and dip into it a loop of Pt wire holding a borax bead; then heat the bead in the blow-pipe flame, which is colored green if the liquid contain $\frac{1}{100}$ of glycerol.

The glycerol used for medicinal purposes should respond to the following tests: (1) its sp. gr. should not vary much from that given above; (2) it should not rotate polarized light; (3) it should not turn brown when heated with sodium nitrate; (4) it should not be colored by H_2S ; (5) when dissolved in its own weight of alcohol, containing one per cent. of H_2SO_4 , the solution should be clear; (6) when mixed with an equal volume H_2SO_4 , of sp. gr. 1.83, it should form a limpid, brownish mixture, but should not give off gas.

POLYATOMIC, OR POLYHYDRIC ALCOHOLS.

Tetratomic Alcohols contain four hydroxyls. The best known is:

Erythrol—*Erythrite*—*Phycite*—*Erythroglucin*— $\text{CH}_2\text{OH}-(\text{CHOH})_2\cdot\text{CH}_2\text{OH}$ —which is a product of decomposition of **erythrin**, $\text{C}_{20}\text{H}_{22}\text{O}_{10}$, which exists in the lichens of the genus *rocella*. It crystallizes in large, brilliant prisms; very soluble in H_2O and in hot alcohol, almost insoluble in ether; sweetish in taste; its solutions neither affect polarized light, nor reduce Fehling's solution, nor are capable of fermentation. Its watery solution, like that of sugar, is capable of dissolving a considerable quantity of lime, and from this solution alcohol precipitates a definite compound of erythrite and calcium. By oxidation with platinum-black it yields **erythroglucic acid**, $\text{C}_4\text{H}_8\text{O}_6$. With fuming HNO_3 it forms a tetranitro compound, which explodes under the hammer.

Pentatomic, or Pentahydric Alcohols—**Pentites**—contain five

hydroxyls. The only member of the group known to exist in nature is the simplest $C_5H_7(OH)_5$, called **adonite**, obtained from *Adonis vernalis*. Other members of the series are obtained by reduction of the corresponding aldopentoses (p. 310).

Hexatomic, or Hexahydric Alcohols—Hexites—contain six hydroxyls. They are closely related to the sugars (p. 311), which they resemble in their properties, although they do not reduce Fehling's solution, and are not fermented by yeast. They are obtained by reduction of the corresponding glucoses, aldohexoses and ketohexoses (p. 314). Three hexites occur in nature:

Mannitol—Mannite— $CH_2OH.(CHOH)_4.CH_2OH$ —constitutes the greater part of manna, and also exists in a number of other plants. It is also produced during the so-called mucic fermentation of sugar, and during lactic fermentation. It crystallizes in long prisms, odorless, sweet; fuses at 166° (330.8° F.) and crystallizes on cooling; boils at 200° (396° F.), at which temperature it is converted into **mannitan**, $C_6H_{12}O_5$; soluble in H_2O , very sparingly in alcohol. When oxidized it yields first mannonic, then mannosaccharic acid (p. 346), and finally, oxalic acid. Organic acids combine with it to form esters.

Sorbitol—Sorbite—occurs in mountain-ash berries. It forms crystals, soluble in water.

Dulcitol—Dulcite—Melampyrite—Dulcose—Dulcin—exists in *melampyrum nemorosum*. It forms colorless, transparent prisms, fuses at 182° (359.6° F.), is odorless, faintly sweet, neutral in reaction, and optically inactive. It is subject to decompositions very similar to those to which mannite is subject, yielding **dulcitan**, $C_6H_{12}O_5$.

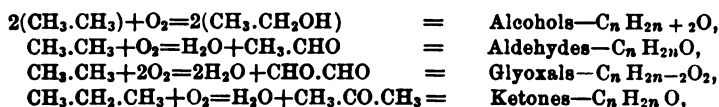
Heptatomic, Octatomic and Nonatomic Alcohols, containing respectively seven, eight and nine hydroxyls, are also known.

All polyatomic alcohols in solutions alkalized with caustic soda, when agitated with benzoyl chlorid, form insoluble benzoic esters, and, under proper conditions, the separation is quantitative, a fact which is utilized for their separation. The diamins (p. 385) behave similarly with benzoyl chlorid.

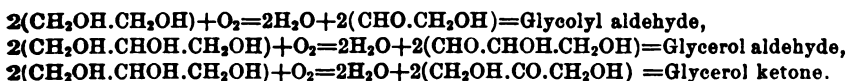
ALDEHYDES AND KETONES.

The pure aldehydes and ketones, containing only CHO or CO and hydrocarbon groups, are to be considered rather as the second products of oxidation of the paraffins than as the first products of oxidation of the alcohols, primary or secondary. While the distinction is not material with the aldehydes derivable from the monoatomic alcohols, it is so with similar derivatives of alcohols of higher atom-

icity and with the ketones, which may be either pure aldehydes or ketones, or, if they retain alcoholic groups, substances of mixed function: aldehyde-alcohols and ketone-alcohols. Thus from the hydrocarbons the following may be derived:



and from the alcohols not only the above, but also substances such as



The aldehydes and ketones are isomeric with each other and also with the allyl alcohols, $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$, and the methylene oxids, $(\text{CH}_2)_x:\text{O}$.

Both aldehydes and ketones contain the carbonyl group CO , which in the ketone is united to two alkyls, $\text{CH}_3.\text{CO}.\text{CH}_3$; and in the aldehyde to one alkyl and a hydrogen atom, $\text{CH}_3.\text{CO}.\text{H}$.

Because of the presence of this oxygen atom, doubly linked to carbon, both aldehydes and ketones form addition products with hydrogen, the former to produce primary, and the latter secondary alcohols: $\text{CH}_3.\text{CHO} + \text{H}_2 = \text{CH}_3.\text{CH}_2\text{OH}$, and $\text{CH}_3.\text{CO}.\text{CH}_3 + \text{H}_2 = \text{CH}_3.\text{CHOH}.\text{CH}_3$. The aldehydes, in which the $\text{C}:\text{O}$ is in a terminal group, also form other addition products mentioned below.

Aldehydes and ketones are acted upon by phosphorus pentachlorid to form compounds in which oxygen is replaced by the halogen. Thus acetic aldehyde yields ethidene chlorid, or dichlorethane: $\text{CH}_3.\text{CHO} + \text{PCl}_5 = \text{CH}_3.\text{CHCl}_2 + \text{POCl}_3$; and acetone yields β dichloropropane: $\text{CH}_3.\text{CO}.\text{CH}_3 + \text{PCl}_5 = \text{CH}_3.\text{CCl}_2.\text{CH}_3 + \text{POCl}_3$.

All aldehydes and ketones condense with hydroxylamin to form oxims (p. 409): $\text{CH}_3.\text{CHO} + \text{NH}_2.\text{OH} = \text{CH}_3.\text{CH}:\text{N}.\text{OH} + \text{H}_2\text{O}$, and with phenylhydrazin to form hydrazones and osazones (p. 485). Both of these reactions are extensively used for the identification of substances containing the $\text{C}:\text{O}$ group.

The aldehydes and ketones may be considered as derivatives of formic aldehyde, $\text{O}:\text{C} \begin{smallmatrix} \text{H} \\ \diagup \diagdown \\ \text{H} \end{smallmatrix}$, alkyls being substituted for one H atom only in the aldehydes: $\text{O}:\text{C} \begin{smallmatrix} \text{CH}_3 \\ \diagup \diagdown \\ \text{H} \end{smallmatrix}$, and for both in the ketones: $\text{O}:\text{C} \begin{smallmatrix} \text{CH}_3 \\ \diagup \diagdown \\ \text{CH}_3 \end{smallmatrix}$.

ALDEHYDES.

The name "aldehyde" is a contraction of "alcohol dehydrogen-**atum**," derived from the method of formation of these bodies by removal of hydrogen from alcohol.

The aldehydes are formed: (1) By the limited oxidation of the corresponding alcohols: $2\text{CH}_3.\text{CH}_2\text{OH} + \text{O}_2 = 2\text{CH}_3.\text{CHO} + 2\text{H}_2\text{O}$; (2) By the action of nascent hydrogen upon the corresponding acidyl chlorids (p. 352), or anhydrids (p. 351): $\text{CH}_3.\text{CO}.\text{Cl} + \text{H}_2 = \text{CH}_3.\text{CHO} + \text{HCl}$, or $(\text{CH}_3.\text{CO})_2\text{O} + 2\text{H}_2 = 2\text{CH}_3.\text{CHO} + \text{H}_2\text{O}$; (3) By the distillation of a mixture of calcium formate and the Ca salt of the corresponding acid: $(\text{H}.\text{COO})_2\text{Ca} + (\text{CH}_3.\text{COO})_2\text{Ca} = 2\text{CO}_3\text{Ca} + 2\text{CH}_3.\text{CHO}$.

The aldehydes, being intermediate between the alcohols and acids, are readily converted into the former by the action of reducing agents: $\text{CH}_3.\text{CHO} + \text{H}_2 = \text{CH}_3.\text{CH}_2\text{OH}$; or into the latter by oxidation: $2\text{CH}_3.\text{CHO} + \text{O}_2 = 2\text{CH}_3.\text{COOH}$. The facility with which the aldehydes are oxidized renders them active reducing agents.

They combine with the monometallic alkaline sulfites to form crystalline compounds, whose formation is frequently resorted to for their separation and purification: $\text{CH}_3.\text{CHO} + \text{SO}_3\text{HNa} = \text{CH}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{SO}_3\text{Na} \end{smallmatrix}$.

They unite directly with ammonia to produce crystalline compounds called aldehyde ammonias (p. 409): $\text{CH}_3.\text{CHO} + \text{NH}_3 = \text{CH}_3.\text{CH} \begin{smallmatrix} \text{HO} \\ \text{NH}_2 \end{smallmatrix}$.

Chlorin and bromin displace the hydrogen of the aldehydic group with formation of acidyl chlorids or bromids: $\text{CH}_3.\text{CHO} + \text{Cl}_2 = \text{CH}_3.\text{CO}.\text{Cl} + \text{HCl}$. The oxygen of the same group may also be displaced by chlorin, by the action of phosphorus pentachlorid, with formation of paraffin dichlorids: $\text{CH}_3.\text{CHO} + \text{PCl}_5 = \text{CH}_3.\text{CHCl}_2 + \text{POCl}_3$. By indirect means compounds may also be obtained in which the hydrogen of the hydrocarbon group is substituted by chlorin, as chloral is obtained from ethylic alcohol: $\text{CH}_3.\text{CH}_2\text{OH} + 4\text{Cl}_2 = \text{CCl}_3.\text{CHO} + 5\text{HCl}$.

The aldehydes polymerize readily, forming cyclic compounds, as trioxymethylene is formed by formic aldehyde: $3\text{H}.\text{CHO} = \text{O} \begin{smallmatrix} \text{CH}_2.\text{O} \\ \text{CH}_2.\text{O} \end{smallmatrix} \text{CH}_2$. Or two aldehyde molecules may condense, by union through carbon atoms, to form **oxyaldehydes** (p. 308), as aldol is formed by condensation of acetic aldehyde: $2\text{CH}_3.\text{CHO} = \text{CH}_3.\text{CHOH}.\text{CH}_2.\text{CHO}$.

Hydrocyanic acid combines with the aldehydes (and ketones) to produce **oxycyanids**, or nitrils of the oxyacids: $\text{CH}_3.\text{CHO} + \text{HCN} = \text{CH}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$, which, in turn, are decomposable by acids or alkalies with formation of the α -oxyacids (p. 340).

Formaldehyde—*Formyl hydrid*— $\text{H}.\text{CHO}$ —30—is formed when air charged with vapor of methylic alcohol is passed over an incandescent platinum wire. It is also produced by the dry distillation of calcium formate: $(\text{H}.\text{COO})_2\text{Ca} = \text{CaCO}_3 + \text{H}.\text{COH}$. By strong cooling, it condenses to a colorless liquid, which boils at -21° (-5.8° F.). It

has a sharp, penetrating odor, and is an active germicide. It is extensively used as an antiseptic and disinfectant, either in the gaseous form or in aqueous solution. The commercial **formaline** is a 40 per cent solution.

Formic aldehyde is probably produced as an intermediate product in plant nutrition, when carbon dioxide is decomposed by the green pigment, **chlorophyll**, under the influence of sunlight, with liberation of oxygen: $\text{CO}_2 + \text{H}_2\text{O} = \text{H}.\text{CHO} + \text{O}_2$, and when so produced it may readily polymerize to form hexoses (p. 311): $6\text{H}.\text{CHO} = \text{C}_6\text{H}_{12}\text{O}_6$.

Formaldehyde polymerizes with great readiness by moderate elevation of temperature to form **paraformaldehyde**, or **trioxymethylene**, $\text{O} \begin{smallmatrix} \text{CH}_2.\text{O} \\ \text{CH}_2.\text{O} \end{smallmatrix} \text{CH}_2$, which is also obtained as a crystalline substance, fusing at 152° (305.6°F.), insoluble in H_2O , alcohol and ether, by distilling glycolic acid with H_2SO_4 , or by the action of silver oxalate or oxid on methene iodide: $\text{CH}_2\text{I}_2 + \text{Ag}_2\text{O} = \text{H}.\text{CHO} + 2\text{AgI}$.

Formic aldehyde reacts with a great variety of substances, and, in reactions at elevated temperatures may advantageously be replaced by the solid trioxymethylene, which is then dissociated. Like all aldehydes (and it is doubly an aldehyde: $\text{O}:\text{C} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$), it is an active reducing agent. With caustic alkalis it forms methyl alcohol and a formate: $2\text{H}.\text{CHO} + \text{NaHO} = \text{H}.\text{CH}_2\text{OH} + \text{H}.\text{COONa}$, or, in the presence of CuO , a formate and hydrogen: $\text{H}.\text{CHO} + \text{NaHO} = \text{H}.\text{COONa} + \text{H}_2$. Calcium hydroxide and other basic hydroxides, by prolonged contact, cause its polymerization to **formose** (p. 314): $6\text{H}.\text{CHO} = \text{C}_6\text{H}_{12}\text{O}_6$. With ammonia it forms hexamethylene tetramine (p. 409); and with ammoniacal salts it forms a variety of complex amines and nitriles (pp. 380, 393).

An extremely valuable property of formic aldehyde is the facility with which it parts with its oxygen atom, by reason of which it readily enters into condensations, uniting other molecule-remainders through the bivalent group CH_2 .

A condensation is the formation of a new molecule by the union of the remainders of two or more others, with the splitting off of water, alcohol, or some other substance. A condensation differs from a *polymerization* in that in the latter nothing is split off, and all the substances involved are polymeres of each other. Sometimes condensations are effected by simple contact of the reacting substances at more or less elevated temperatures; but, more usually, the presence of another substance, acting as a contact agent, is required. Substances acting in this manner are quite numerous, and are called **condensing agents**. Probably the most important are aluminium, ferric and zinc chlorides, hydrochloric and sulfuric acids, sodium acetate and ethylate, pyridin, and piperidin.

As examples of the simplest condensations with formic aldehyde we may mention the two following: With alcohols it condenses to produce formals (p. 306): $2\text{H}.\text{CH}_2\text{OH} + \text{H}.\text{CHO} = \text{CH}_3.\text{O}.\text{CH}_2.\text{O}.\text{CH}_3 + \text{H}_2\text{O}$. With secondary amins (p. 377) it condenses to form alkyl diamins (p. 380): $2\text{R}'_2\text{NH} + \text{H}.\text{CHO} = \text{R}'_2\text{N}.\text{CH}_2.\text{NR}'_2 + \text{H}_2\text{O}$; an action which is particularly marked with aromatic amins (p. 470): $2\text{C}_6\text{H}_5.\text{NH}_2 + \text{H}.\text{CHO} = \text{C}_6\text{H}_5.\text{NH}.\text{CH}_2.\text{NH}.\text{C}_6\text{H}_5 + \text{H}_2\text{O}$. Other instances of the condensing action of formic aldehyde will be considered later.

The presence of formic aldehyde, which is now frequently added to milk and other articles of food, may be recognized by the following reactions, after distillation, if necessary: (1) Heat with 0.5 cc. dimethylanilin and a few drops H_2SO_4 on the water-bath for half an hour; add excess of alkali; expel excess of dimethylanilin with a current of steam; filter; place the filter in a porcelain capsule and moisten it with acetic acid; add a trace of lead peroxid, and warm: an intense blue color (p. 503). (2) Add the liquid (distillate) to an equal volume of aqueous solution of anilin (3:1000): a white ppt. (3) Dissolve 0.01 morphin hydrochlorid in 1 cc. concentrated H_2SO_4 , and mix two drops of this and suspected solutions: an intense rose-violet color.

Acetaldehyde—Acetic Aldehyde—Acetyl hydrid— $\text{CH}_3.\text{CHO}$ —44—is formed in all reactions in which alcohol is deprived of H without introduction of O. It is prepared by distilling from a capacious retort, connected with a well-cooled condenser, a mixture of H_2SO_4 , 6 pts.; H_2O , 4 pts.; alcohol, 4 pts., and powdered manganese dioxid, 6 pts. The product is redistilled from calcium chlorid below 50° (122° F.). The second distillate is mixed with two volumes of ether, cooled by a freezing mixture, and saturated with dry NH_3 ; there separate crystals of **aldehyde ammonia**, $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{NH}_2 \\ \text{OH} \end{smallmatrix}$, which are washed with ether, dried and decomposed in a distilling apparatus, over the water-bath, with the proper quantity of dilute H_2SO_4 ; the distillate is finally dried over calcium chlorid and rectified below 35° (95° F.).

Acetic aldehyde is also formed by heating acetylene with vapor of water: $\text{CH}:\text{CH} + \text{H}_2\text{O} = \text{CH}_3.\text{CHO}$ (p. 288).

Aldehyde is a colorless, mobile liquid; has a strong, suffocating odor; sp. gr. 0.790 at 18° (64.4° F.); boils at 21° (69.8° F.); soluble in all proportions in water, alcohol and ether. If perfectly pure, it may be kept unchanged; but if an excess of acid have been used in its preparation, it gradually decomposes. When heated to 100° (212° F.), it is decomposed into water and crotonic aldehyde.

In the presence of nascent H, aldehyde takes up H_2 , and regenerates alcohol. Cl converts it into acetyl chlorid, $\text{C}_2\text{H}_3\text{O}.\text{Cl}$, and other products. Oxidizing agents convert it into acetic acid. At the ordinary temperature H_2SO_4 ; HCl ; and SO_2 convert it into a

colorless liquid called **paraldehyde** $(C_2H_4O)_3$, which boils at 124° (255.2° F.), and is more soluble in cold than in warm water. The same reagents, acting upon aldehyde at temperatures below 0° (32° F.) convert it into **metalddehyde** $(C_2H_4O)_n$. When heated with potassium hydroxid, aldehyde becomes brown, a brown resin separates, and the solution contains potassium formate and acetate. If a watery solution of aldehyde be treated, first with NH_3 and then with H_2S , a solid, crystalline base, **thialdin**, $C_6H_{13}NS_2$, separates. It also forms crystalline compounds with the alkaline bisulfites. It decomposes solutions of silver nitrate, separating the silver in the metallic form, and under conditions which cause it to adhere strongly to glass.

Vapor of aldehyde, when inhaled in a concentrated form, produces **asphyxia**, even in comparatively small quantity. When diluted with air it is said to act as an anæsthetic. When taken internally it causes sudden and deep intoxication, and it is to its presence that the first products of the distillation of spirits of inferior quality owe in a great measure their rapid, deleterious action.

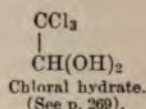
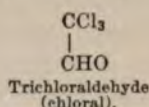
Trichloraldehyde — *Trichloracetyl hydrid* — **Chloral** — $CCl_3.CHO$ — 147.5 — is one of the final products of the action of Cl upon alcohol, and is obtained by passing dry Cl through absolute alcohol to saturation; applying heat toward the end of the reaction, which requires several hours for its completion. The liquid separates into two layers; the lower is removed and shaken with an equal volume of concentrated H_2SO_4 and again allowed to separate into two layers; the upper is decanted; again mixed with H_2SO_4 , from which it is distilled; the distillate is treated with quicklime, from which it is again distilled, that portion which passes over between 94° and 99° (201.2° – 210.2° F.) being collected. It sometimes happens that chloral in contact with H_2SO_4 is converted into a modification, insoluble in H_2O , known as **metachloral**; when this occurs it is washed with H_2O , dried and heated to 180° (356° F.), when it is converted into the soluble variety, which distils over.

The formation of chloral from alcohol does not progress according to the simple equation: $CH_3.CH_2OH + 4Cl_2 = CCl_3.CHO + 5HCl$, but passes through several stages. First, the alcohol is oxidized to aldehyde: $CH_3.CH_2OH + Cl_2 = CH_3.CHO + 2HCl$. This reacts with alcohol to produce acetal (p. 306): $CH_3.CHO + 2CH_3.CH_2OH = CH_3.CH(OC_2H_5)_2 + H_2O$. This is then converted into trichloroacetal: $CH_3.CH(OC_2H_5)_2 + 3Cl_2 = CCl_3.CH(OC_2H_5)_2 + 3HCl$. This, by the action of the hydrochloric acid formed in the last reaction, yields chloral alcoholate and ethyl chlorid: $CCl_3.CH(OC_2H_5)_2 + HCl = CCl_3.CH\begin{smallmatrix} OH \\ \diagdown \\ O.C_2H_5 \end{smallmatrix} + C_2H_5Cl$. And from the former chloral is liberated by sulfuric acid: $CCl_3.CH\begin{smallmatrix} OH \\ \diagdown \\ O.C_2H_5 \end{smallmatrix} + H_2SO_4 = CCl_3.CHO + (C_2H_5)HSO_4 + H_2O$.

Chloral is a colorless liquid, unctuous to the touch; has a penetrating odor and an acrid, caustic taste; sp. gr. 1.502 at 18° (64.4° F.); boils at 97° (206.6° F.), very soluble in water, alcohol, and ether; dissolves Cl, Br, I, S, and P. Its vapor is highly irritating. It distills without alteration.

Although chloral has not been obtained by the direct substitution of Cl for H in aldehyde, its reactions show it to be an aldehyde. It forms crystalline compounds with the bisulfites; it reduces solutions of silver nitrate in the presence of NH_3 ; NH_3 and H_2S form with it a compound similar to thialdin; with nascent H it regenerates aldehyde; oxidizing agents convert it into trichloroacetic acid. Alkaline solutions decompose it with formation of chloroform and a formate.

With a small quantity of H_2O chloral forms a solid, crystalline hydrate, heat being at the same time liberated. This hydrate has the composition $\text{C}_2\text{HCl}_3\text{O} \cdot \text{H}_2\text{O}$, and its constitution, as well as that of chloral itself, is indicated by the formulæ:



Chloral Hydrate—Chloral (U. S.)—is a white, crystalline solid; fuses at 57° (134.6° F.); boils at 98° (208.4° F.), at which temperature it suffers partial decomposition into chloral and H_2O ; volatilizes slowly at ordinary temperatures; is very soluble in H_2O ; neutral in reaction; has an ethereal odor, and a sharp, pungent taste. Concentrated H_2SO_4 decomposes it with formation of chloral and **chloralid**. HNO_3 converts it into trichloroacetic acid. When pure it gives no precipitate with silver nitrate solution, and is not browned by contact with concentrated H_2SO_4 . Under the influence of sunlight it is violently decomposed by potassium chlorate, which oxidizes it in part to trichloroacetic acid; chlorin, phosgene gas, carbon dioxide, and chloroform are given off, and after a time, crystals of potassium trichloroacetate separate from the cooled mixture.

Chloral also combines with alcohol, with elevation of temperature, to form a solid, crystalline body—**chloral alcoholate**:
 $\text{CCl}_3\text{CH} \begin{array}{l} \text{OH} \\ \diagup \\ \text{O}-\text{C}_2\text{H}_5 \end{array}$

Action of Chloral Hydrate upon the Economy.—Although it was the ready decomposition of chloral into a formate and chloroform which first suggested its use as a hypnotic to Liebreich, and although this decomposition was at one time believed to occur in the body under the influence of the alkaline reaction of the blood, more recent investigations have shown that the formation of chloroform from chloral in the blood is, to say the least, highly improbable, and that

chloral has, in common with many other chlorinated derivatives of this series, the property of acting directly upon the nerve-centers.

Neither the urine nor the expired air contains chloroform when chloral is taken internally; and when taken in large doses, chloral appears in the urine. The fact that the action of chloral is prolonged for a longer period than that of the other chlorinated derivatives of the fatty series is probably due, in a great measure, to its less volatility and less rapid elimination.

When taken in overdose, chloral acts as a poison, and its use as such is rapidly increasing as acquaintance with its powers becomes more widely disseminated. A strong aqueous solution is frequently added by criminals to intoxicants to deprive their victims of consciousness (knock-out drops).

No chemical antidote is known. The treatment should be directed to the removal of any chloral remaining in the stomach by the syphon, and to the maintenance or restoration of respiration.

In fatal cases of poisoning by chloral that substance may be detected in the blood, urine, and contents of the stomach by the following method: the liquid is rendered strongly alkaline with potassium hydroxid: placed in a flask, which is warmed to 50° – 60° (122° – 140° F.), and through which a slow current of air, heated to the same temperature, is made to pass; the air, after bubbling through the liquid, is tested for chloroform by the methods described on page 279. As chloral distils with vapor of water from acid solutions, and as it gives the same reactions as chloroform, except the fluorescence with the resorcinol reaction (p. 279), the presence of chloral as such can only be positively demonstrated by extraction of the crystals of the hydrate by ether, and spontaneous evaporation of the ethereal solution.

Bromal— CBr_3CHO —281.—A colorless, oily, pungent liquid: sp. gr. 3.34; boils at 172° (341.6° F.); neutral; soluble in H_2O , alcohol, and ether. It combines with H_2O to form bromal hydrate, $\text{CBr}_3\text{CH(OH)}_2$; large transparent crystals; soluble in H_2O ; decomposed by alkalis into bromoform and a formate. Produces anæsthesia without sleep; very poisonous.

Thioaldehydes.—By the action of H_2S on aldehyde in the presence of HCl two products are obtained, having the composition $(\text{CH}_3\text{CHS})_3$, known as α and β Trithioacetaldehyde. The former is in large prismatic crystals, fusible at 101° (213.8° F.), the latter in long needles, fusible at 125° – 126° (257° – 258.8° F.).

Propaldehyde—Propionic aldehyde— $\text{CH}_3\text{CH}_2\text{CHO}$ —58—obtained by the general reaction from propylic alcohol, is a colorless liquid, resembling acetic aldehyde; boils at 40° (120.2° F.).

Normal Butaldehyde—Butyric aldehyde— $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ —

72—is an oily liquid, boiling at 73° (163.2° F.). Its trichlorinated derivative, **Trichlorobutaldehyde**, or **Butyric chloral**, $\text{CCl}_3.\text{CH}_2.\text{CH}_2.\text{CHO}$ —is the substance whose hydrate is used as a medicine under the name **croton chloral hydrate**. It is a colorless liquid, b.p. 160° , obtained by the action of Cl on acetaldehyde.

Acetals—Formals.—These are ester-like bodies (p. 358) corresponding to the hypothetical aldehyde hydrates: $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$, which are themselves incapable of existence, except they contain a halogen, as in chloral hydrate: $\text{CCl}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$. The acetals have the general formula: $\text{R}'.\text{CH} \begin{smallmatrix} \text{OR}' \\ \text{OR}' \end{smallmatrix}$, and the formals the structure: $\text{CH}_2 \begin{smallmatrix} \text{OR}' \\ \text{OR}' \end{smallmatrix}$, in which R' represents an alkyl. The acetals are produced by oxidation of the alcohols by MnO_2 and H_2SO_4 . Thus, $6\text{CH}_3.\text{CH}_2\text{OH} + \text{O}_2 = 2\text{CH}_3.\text{CH}(\text{OC}_2\text{H}_5)_2 + 4\text{H}_2\text{O}$, and by other methods. The formals are formed by condensation, in presence of H_2SO_4 , or of Fe_2Cl_6 , of alcohols and formic aldehyde: $2\text{CH}_3.\text{CH}_2\text{OH} + \text{H}.\text{CHO} = \text{CH}_3.\text{CH}_2.\text{O}.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_3 + \text{H}_2\text{O}$.

The formation of acetals and formals is utilized in the preparation of certain aldehydes, such as glyceric aldehyde. By hydrolysing agents, as by heating with aqueous HCl , they are split into their components: $\text{CH}_3.\text{CH}(\text{O}.\text{C}_2\text{H}_5)_2 + \text{H}_2\text{O} = \text{CH}_3.\text{CHO} + 2\text{CH}_3.\text{CH}_2\text{OH}$.

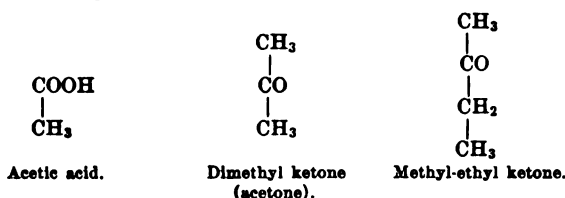
Methylal—Formal— $\text{CH}_2 \begin{smallmatrix} \text{OCH}_3 \\ \text{OCH}_3 \end{smallmatrix}$ —76—is formed by distilling a mixture of MnO_2 , methyl alcohol, H_2SO_4 and H_2O . It is a colorless liquid; sp. gr. 0.8551 at 17° (62.6° F.); boiling at 42° (107.6° F.); soluble in H_2O , alcohol, and oils. It has a burning, aromatic taste, and an odor resembling those of chloroform and acetic acid. It has been used as a hypnotic.

Acetal— $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix}$ —104—a colorless liquid, boils at 104° (219.2° F.), sp. gr. 0.8314; sparingly soluble in H_2O , readily in alcohol; obtained by heating a mixture of aldehyde, alcohol and glacial acetic acid, or in the same manner as formal, using ethylic in place of methylic alcohol.

Dialdehydes—containing two CHO groups, such as **Glyoxal**— $\text{CHO}.\text{CHO}$, are also known. Glyoxal is formed by the limited oxidation of acetic aldehyde by nitric acid: $\text{CH}_3.\text{CHO} + \text{O}_2 = \text{CHO}.\text{CHO} + \text{H}_2\text{O}$. But it has not been obtained pure, containing oxalic and formic acids as impurities. It is very soluble in water, and has the chemical properties common to the aldehydes. By the action of hydrolysing agents, such as BaH_2O_2 , or CaH_2O_2 , one aldehyde group is oxidized to a carboxyl, and the other is reduced to a methoxyl: $\text{CHO}.\text{CHO} + \text{H}_2\text{O} = \text{CH}_2\text{OH}.\text{COOH}$. When warmed with ammonia and formic aldehyde it produces glyoxalin by condensation (p. 514).

KETONES OR ACETONES.

The ketones, or acetones, contain the group $C:O:$, linking two hydrocarbon groups; or they may be considered as derived from the hydrocarbons by substitution of O for H_2 in a CH_2 group. The **monoketones** contain one CO group, the **diketones** two, etc. The $(CO)''$ group also occurs in the aldehydes, in which, however, it is linked with H, $(O:C.H)'$, and in the carboxyl group, in which it is linked with OH, $(O:C.OH)'$, in both cases occupying a terminal position. while in ketones, ketonic acids, etc., its position is intermediate. Ketones are symmetrical if the two alkyls united by CO are similar, unsymmetrical if they are different:



Ketones are isomeric with and closely allied to the aldehydes, from which they differ chiefly in that: (1) They are not so easily oxidized, do not reduce alkaline solutions of silver salts, and, on oxidation, split at the CO group to form a carboxylic acid or acids, or ketones, of less carbon content: $CH_3.CO.CH_3 + 2O_2 = CH_3.COOH + CO_2 + H_2O$; (2) Nascent hydrogen converts them into secondary alcohols by addition: $CH_3.CO.CH_3 + H_2 = CH_3.CHOH.CH_3$. (3) The ketones do not polymerize; (4) Only those ketones which contain a methyl group form crystalline compounds with alkaline bisulfites.

The monoketones are produced: (1) By oxidation of the secondary alcohols: $2CH_3.CHOH.CH_3 + O_2 = 2CH_3.CO.CH_3 + 2H_2O$; (2) By distillation of the calcium salts of the fatty acids: $Ca(CH_3.COO)_2 = CH_3.CO.CH_3 + CaCO_3$; (3) By decomposition of ketonic acids (p. 347): $CH_3.CO.CH_2.COOH = CO_2 + CH_3.CO.CH_3$; (4) By the interaction of zinc alkyls (p. 375) and acidyl halids (p. 352): $Zn(CH_3)_2 + 2CH_3.CO.Cl = 2CH_3.CO.CH_3 + ZnCl_2$; (5) By the action of sodium upon a mixture of acidyl and alkyl halids: $CH_3.CO.Cl + CH_3I = CH_3.CO.CH_3 + NaCl + NaI$.

Dimethyl Ketone—Acetone—Acetylmethylid—Pyroacetic ether or spirit— $CO \begin{array}{l} \diagup CH_3 \\ \diagdown CH_3 \end{array}$ —58—is formed as one of the products of the dry distillation of the acetates; by the decomposition of the vapor of acetic acid at a red heat; by the dry distillation of sugar, tartaric acid, etc.; and in a number of other reactions. It is obtained by distilling dry calcium acetate. It is also formed in large quantity in the preparation of anilin.

It is a limpid, colorless liquid; sp. gr. 0.7921 at 18° (64.4° F.); boils at 56° (132.8° F.); soluble in H₂O, alcohol and ether; has a peculiar ethereal odor and a burning taste; is a good solvent of resins, fats, camphor, gun-cotton; readily inflammable. It forms crystalline compounds with the alkaline bisulfites. Cl and Br, in the presence of alkalis, convert it into chloroform or bromoform; Cl alone produces with acetone a number of chlorinated products of substitution. Certain oxidizing agents transform it into a mixture of formic and acetic acids; others into oxalic acid.

Acetone has been found to exist in the blood and urine in certain pathological conditions, and notably in diabetes. The peculiar odor exhaled by diabetics is produced by this substance, which has also been considered as being the cause of the respiratory derangements and coma which frequently occur in the last stages of the disease.

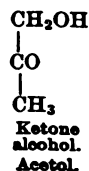
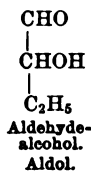
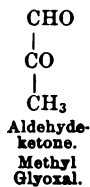
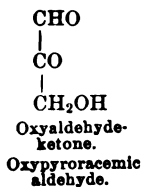
That acetone exists in the blood in such cases is certain: it is not certain, however, that its presence produces the condition designated as *acetonæmia*. It can hardly be doubted that the acetone thus existing in the blood is indirectly formed from diabetic sugar, and it is probable also that a complex acid, known as *ethyldiacetic*, C₆H₈O₃H, is formed as an intermediate product.

See aromatic ketones.

Diketones, containing two CO groups, such as CH₃.CO.CO.CH₃, **triketones**, such as CH₃.CO.CO.CO.CH₃, and **tetraketones**, such as CH₃.(CO)₄.CH₃, are also known.

ALDEHYDE-ALCOHOLS, KETONE-ALCOHOLS, ALDEHYDE-KETONES, AND OXYALDEHYDE-KETONES.

These bodies are, as the names indicate, substances of mixed function. The known oxyaldehyde-ketones, aldehyde-ketones, and such of the aldehyde- and ketone-alcohols as contain hydrocarbon groups are neither numerous nor important. The following formulæ indicate their structure:



The aldehyde-alcohols, such as aldol and glycolyl aldehyde: CH₂OH.CHO, are called **oxyaldehydes**; and the ketone-alcohols such as acetol are called **ketols**.

CARBOHYDRATES.

The definition of the term **carbohydrate** as "a substance of unknown constitution composed of carbon, hydrogen and oxygen, in which the oxygen and hydrogen are in the same proportion as in water" was self-destructive so soon as the constitution of these substances should become known, as it now has. Yet the first words of the definition were necessary to exclude substances such as acetic acid, $C_2H_4O_2$, which would otherwise accord with the definition, yet were never considered as carbohydrates. But, while the sugars and starches have been thus removed from the "miscellaneous" residuum of our chemical classification, they are still conveniently referred to as carbohydrates in physiological chemistry.

The simplest of the carbohydrates are oxyaldehydes or ketols in which all the groups, other than the aldehyde or ketone groups, are primary or secondary alcoholic groups; and the more complex consist of two or more molecules of the simpler forms, united with elimination of water.

The carbohydrates are classified into:

Monosaccharids, or Monoses—which do not yield any other sugar or sugars by the action upon them of dilute acids (glucose, fructose, galactose, etc.);

Disaccharids, or Saccharobioses—which, under the influence of dilute acids, take up H_2O and yield two other sugar molecules (saccharose, lactose, maltose, etc.);

Trisaccharids, or Saccharotrioses—which, under the same influence, take up $2H_2O$ and yield three other sugar molecules; and

Polysaccharids—which, under the same influence, take up more than $2H_2O$, and yield more than three sugar molecules (starches, gums, celluloses, etc.).

The disaccharids, trisaccharids and polysaccharids may be considered as produced by the fusion of two or more monosaccharid molecules with elimination of one or more molecules of water.

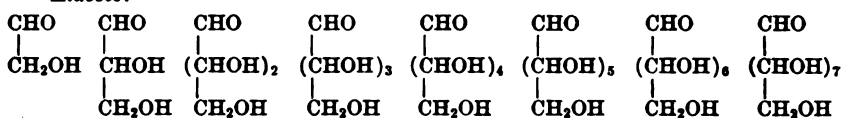
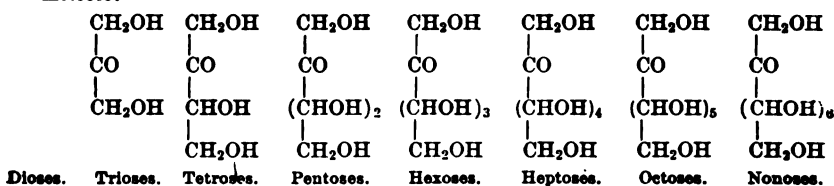
Those carbohydrates which contain the ketone group, CO , are called **ketoses**, those containing the aldehyde group, CHO , **aldoses**. The names of all carbohydrates terminate in **ose**.

MONOSACCHARIDS—MONOSES.

Monosaccharids are **dioses, trioses, tetroses, pentoses, hexoses, heptoses, octoses** or **nonoses** according as they contain from two to nine carbon atoms. (See table on next page.)

The monosaccharids are neutral substances, sweet, odorless, white, insoluble in ether, sparingly soluble in alcohol, and readily soluble in

water. Like all aldehydes and ketones, they are readily oxidized, and in their oxidation act as reducing agents. It is upon this quality that the several "reduction tests," such as Trommer's, Fehling's, Barfoed's, Boettger's Mulder-Neubauer's, etc., are based. Another quality of the monosaccharids, utilized for their separation and identification, is that they all give crystalline precipitates of substances called **osazones** when their solutions, acidulated with acetic acid, are heated with phenyl-hydrazin, $C_6H_5.H:N.N:H_2$. The trioses, hexoses and nonoses are capable of alcoholic fermentation, the others are not. Most of the monosaccharids are optically active.

Aldoses.**Ketoses.**

Dioses. Trioses. Tetroses. Pentoses. Hexoses. Heptoses. Octoses. Nonoses.

DIOSES, TRIOSSES, TETROSES AND PENTOSSES.

Glycolyl aldehyde, $CH_2OH.CHO$, is the only diose possible. It is produced by the action of baryta water upon brom-acetaldehyde.

Of the two possible trioses **Glyceric aldehyde** is obtained by starting from acrolein acetal. This is oxidized to glyceric acetal: $2CH_2:CH.CH(O.C_2H_5)_2 + 2O_2 + 2H_2O = 2CH_2OH.CHOH.CH(O.C_2H_5)_2$; which is then hydrolyzed: $CH_2OH.CHOH.CH(O.C_2H_5)_2 + H_2O = CH_2OH.CHOH.CHO + 2CH_3.CH_2OH$. **Glycerol ketone**, or **dioxyacetone**, $CH_2OH.CO.CH_2OH$, has also been obtained synthetically. The aldehyde and ketone are formed together when glycerol is oxidized by dilute nitric acid.

Similarly **erythrose** is a mixture of the two **tetroses**, $CHO.(CHOH)_2.CH_2OH$ and $CH_2OH.CHOH.CO.CH_2OH$, formed by oxidation of erythrol by dilute nitric acid.

The **pentoses** hitherto described are all aldo-pentoses, $C_4H_5(OH)_4.CHO$, although keto-pentoses probably also exist. When distilled with hydrochloric or dilute sulfuric acid they yield **furfurole**: $CHO.(CHOH)_3.CH_2OH = 3H_2O + CHO.C \begin{smallmatrix} CH:CH \\ \diagup \quad \diagdown \\ CH.O \end{smallmatrix}$; a reaction which is utilized for their quantitative determination. **Arabinose** is a pen-

tose obtained by the action of dilute sulfuric acid upon cherry gum. **Xylose**, or wood sugar, is produced by boiling wood-gum with dilute acid. **Ribose** is a synthetic product. **Rhamnose**, or **Isodulcitol**, **Chinovose**, and **Fucose** are methyl-pentoses: $\text{CH}_3.(\text{CHOH})_4.\text{CHO}$, obtained by the decomposition of certain glucosids or from sea weeds. These pentoses result from the hydrolysis of pentosanes, polysaccharids occurring as gums in plants. Pentoses have also been found in the urine, particularly in diabetes and after the use of certain fruits containing pentosanes. They are also among the products of decomposition of certain nucleoproteids. Pentoses, when warmed with hydrochloric acid in presence of phloroglucin, give a fine red color, and a sharp absorption band near the Na line.

HEXOSES—GLUCOSES.

In this class are included some well-known sugars, such as glucose and fructose, which occur free in the vegetable world. They exist in ether-like combination in many of the glucosids (p. 465).

They are mostly sweet, crystalline substances, very soluble in water, and difficultly soluble in alcohol. They are formed by (1) the hydrolysis of the di- and polysaccharids: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = 2\text{C}_6\text{H}_{12}\text{O}_6$; (2) by oxidation of the corresponding hexatomic alcohol; (3) by reduction of the lactones of the monocarboxylic acids (p. 368).

They exhibit the usual reactions of the alcohols and those of the aldehydes or ketones. On reduction they produce hexatomic alcohols; and on oxidation they yield monocarboxylic acids. Their alcoholic hydrogen is replaceable by certain metals with formation of **saccharates**, corresponding to the alcoholates (p. 286). With acids they yield esters. They form **osazones** with phenylhydrazin. Some are very prone to alcoholic fermentation: $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_2\text{H}_6\text{O} + 2\text{CO}_2$, while others readily undergo lactic fermentation: $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_3\text{H}_6\text{O}_3$. Being polyatomic alcohols, the hexoses form insoluble benzoic esters when their alkaline solutions are shaken with benzoyl chlorid (p. 298).

Of the described hexoses, mannose, glucose, gulose, idose, galactose and talose are aldoses; fructose and sorbinose are ketoses.

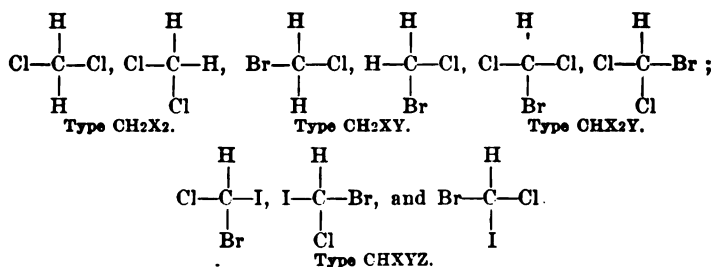
Optical Activity.—All of the hexoses exist in three isomerids, differing from each other in their action upon polarized light. One of these rotates the plane of polarization to the right, and is designated as the dextro-, or d-compound; another is lævogyrous and is designated as the lævo-, or l-compound, while the third is inactive, and is distinguished by the symbol (d+l).

Stereoisomerism, or Space Isomerism.—The graphic formulæ indicate the structure of the molecule only partially; they show that certain atoms in the molecule are attached to some of their fellows

more closely than to others, but they give no indication of the positions which the atoms occupy in space with regard to each other.

The expression $\begin{array}{c} \text{H} \backslash \\ \text{C} - \text{O} - \text{H} \\ \text{H} / \end{array}$, the most completely detailed graphic representation of that group, indicates at the most that the two hydrogen atoms are attached to one side of the carbon atom, while the hydroxyl is attached to another. **Stereochemistry** is that branch of chemistry treating of the relations of the atoms to each other *in space*. It has been greatly developed in recent years and affords, among other things, the first rational explanation of the cause of the differences in the optical activity of the hexoses, as well as of lactic and tartaric acids, and of many other substances.

If we suppose that differences in the relative positions which atoms or groups attached to carbon atoms occupy with relation to each other produce different compounds (see Place Isomerism, p. 339, Orientation, p. 436); and if we also suppose that the four valences of the carbon atom act in a plane, and at right angles to each other, a vast number of space-isomerids of the di- and poly-substituted derivatives of the aliphatic hydrocarbons would exist, no representatives of which are, however, known. For example, marsh-gas would yield two isomerids of each of the types: CH_2X_2 , CH_2XY and $\text{CH}(\text{X})_2\text{Y}$, and three isomerids of the type CHXYZ , in which X, Y, and Z represent any three univalent atoms or radicals, thus:



But only one representative of each of these types is known. Therefore the usual graphic representation of the valences of the carbon atom as above, while convenient, is not *spatially* consistent with fact, and the four valences of the carbon atom are not exerted in one plane.

The suggestion of Van't Hoff (following the somewhat similar idea of Kekulé) that the valences of the carbon atom are represented by considering it as occupying the interior of a regular tetrahedron, the solid angles of which indicate the direction of its valences (Fig. 40, A), taken in connection with the hypothesis of an **asymmetric carbon atom**, affords a rational explanation of the facts just cited,

and of the differences in the optical properties of the substances mentioned.

Admitting the regular tetrahedron to represent the arrangement of the valences of the carbon atom, it follows that all carbon atoms, two of whose valences are satisfied by the same kind of univalent atom or group, and the other two by two constant but dissimilar univalents, must be symmetrical. The two similar univalents must occupy the summits at the extremities of some one crest, and the only possible variation in arrangement of the other two is in their position with regard to this crest. Thus B and C, Fig. 40, although dissimilar in the position in which they are placed, become perfectly symmetrical when either one is rotated through 180 degrees. But when all four of the carbon valences are satisfied by different univalents two arrangements are possible, producing two molecular groups which are unsymmetrical in whatever position they may be placed. Thus D and E, Fig. 40, are unsymmetrical in the positions in which they are represented, and remain so, however their positions may be changed.

A carbon atom attached to four different univalents is called an **asymmetric carbon atom**. In graphic formulæ asymmetric carbon atoms are designated by the italic *C*, or by an asterisk, *C**. Substances containing an asymmetric carbon atom exist in three optical isomerismes: *dextrogyrous* (*d*), *levogyrous* (*l*), and *optically inactive*, or *racemic* (*d*+*l* or *i*, or *r*).

The structure of the four isomeric tartaric acids (p. 344) was first explained under the hypothesis of the asymmetric carbon atom. Let it be assumed that two asymmetric carbon atoms, with their attached groups or atoms, exert a "directing influence" upon each other, and that, being attached to each other at one point only, they are capable

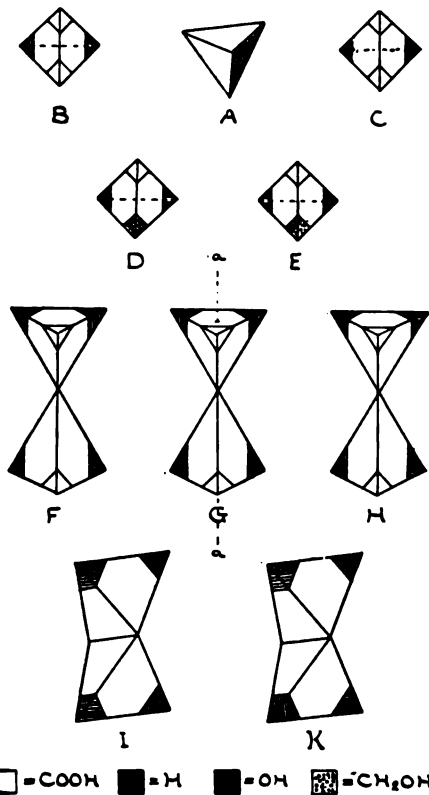


FIG. 40.

of rotating independently about a common axis (*a.a.* Fig. 40, G), such rotation would then occur in obedience to the directing influence until a condition of equilibrium is reached, in which position the atoms would remain. Assuming this position to be that shown in F, G, and H, Fig. 40, with the two COOH groups in like relation, then the three unsymmetrical arrangements shown in the figure are possible. The first represents the structure of dextro-tartaric acid, G that of lævo-tartaric acid, and H that of meso-tartaric acid, while racemic acid is a combination of dextro- and lævo-tartaric acids.

The tetrahedron representation of the carbon valences adapts itself well also to the explanation of certain isomerids of the ethylene series, in which two carbon atoms are doubly linked together. In these the two carbon atoms being linked together at two points (I and K, Fig. 40) cannot be considered as being capable of rotation, and, if the two other valences of each carbon atom are satisfied by the same two dissimilar univalents, two positions are possible: I, in which the like univalents are directed to the same side, called the "plane symmetrical configuration," and K, in which they are directed towards opposite sides, called the "axially symmetrical configuration."

Formose is a synthetic hexose, obtained by polymerization of formic aldehyde: $6\text{H}.\text{CHO}=\text{C}_6\text{H}_{12}\text{O}_6$. **Acrose** is similarly obtained from glyceric aldehyde: $3\text{CH}_2\text{OH}.\text{CHO}=\text{C}_6\text{H}_{12}\text{O}_6$; or by the action of barium hydroxid upon acrolein bromid: $2\text{CH}_2\text{Br}.\text{CHBr}.\text{CHO}+2\text{Ba}.\text{H}_2\text{O}_2=\text{C}_6\text{H}_{12}\text{O}_6+2\text{BaBr}_2$.

Mannose is obtained, as d-, l-, and d+l, mannoses by oxidation of the corresponding mannitols.

Glucose — Grape Sugar — Dextrose — Liver Sugar — Diabetic Sugar—d-Glucose occurs in many sweet fruits and vegetable juices, and in honey, accompanied by fructose; and, in the animal world, in the contents of the intestine, liver, bile, thymus, heart, lungs, blood, and, in small quantity, in the urine. Pathologically, it appears in the saliva, perspiration, fæces, and, in largely increased amount, in the blood and urine in diabetes mellitus. It is produced by the decomposition of the polysaccharids and of many of the glucosids, and is manufactured on a large scale by the action of boiling dilute H_2SO_4 upon starch. The commercial product so obtained is either an amorphous, white solid (grape sugar), containing about 60% of true glucose, along with dextrins and the unfermentable isomaltose, or gallisin, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$; or a thick, colorless syrup (glucose), containing, besides the above, a minute quantity of a nitrogenous body which exerts a solvent action upon coagulated albumin at the body temperature.

d-Glucose has been produced synthetically by the reduction of the lactone of d-gluconic acid (p. 343).

It crystallizes from its aqueous solutions at the ordinary temperature with difficulty in white, opaque, spheroidal masses containing 1Aq, which fuse at 86° and lose the Aq at 110° . From its concentrated aqueous solution at 30° to 35° , or from its alcoholic solution it crystallizes in hard, anhydrous, crystalline crusts, which fuse at 146° . It is soluble in all proportions in hot water, is very soluble in cold water, and soluble in alcohol. It is less sweet and less soluble than cane sugar. Its aqueous solutions are dextrogyrous: $[a]_D = +52.6^{\circ}$ in boiled solutions. Freshly prepared cold aqueous solutions have nearly double that rotary power at first, the value of $[a]_D$ gradually falling to 52.6° in about twenty-four hours. Its osazone, d-glucosazone, crystallizes in needles, fusible at 205° . Its solutions dissolve baryta and lime, with which, as with potash, soda, and the oxids of Pb and Cu, it forms **saccharates**.

l-Glucose is formed by reduction of the lactone of l-gluconic acid. It is in all respects similar to d-glucose except that it fuses at 143° , and its solutions are lævogyrous $[a]_D = -51.4^{\circ}$.

d+l-Glucose is formed by reduction of d+l-gluconic lactone; or by union of d- and l-glucose. Its solutions are optically inactive.

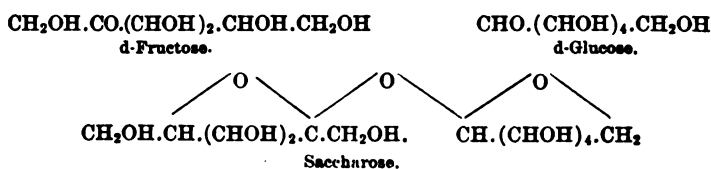
Galactose is also known in its three modifications. d-Galactose is produced by the hydrolysis of milk sugar and of certain gums. It crystallizes more readily than glucose, is very sparingly soluble in cold alcohol, has a specific rotary power of $[a]_D = +83.33^{\circ}$, and fuses at 160° . By reduction it yields dulcete, and by oxidation galactonic acid, $\text{CH}_2\text{OH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$, and mucic acid, $\text{COOH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$. **Cerebrose**, obtained by the hydrolysis of **cerebrin**, a constituent of nerve tissue, is identical with galactose.

Fructose, a ketohexose, exists in the three modifications. *d-Fructose*—*Lævulose*—*Fruit sugar*—forms the uncrystallizable portion of the sugar of fruits and of honey, in which it is associated with glucose; it is produced artificially by the prolonged action of boiling water upon inulin, a polysaccharid; also, along with an equal quantity of glucose, as one of the constituents of invert sugar, by the decomposition of cane sugar; and from d-glucosazone. It crystallizes with great difficulty, fuses at 95° , is very soluble in water, and insoluble in absolute alcohol. Although called d-fructose, because of its formation from d-glucosazone, it is strongly lævogyrous: $[a]_D = -71.4^{\circ}$. It is less readily fermentable than glucose, which it equals in the readiness with which it reduces cupropotassic solutions. With phenylhydrazin it yields d-glucosazone (p. 485).

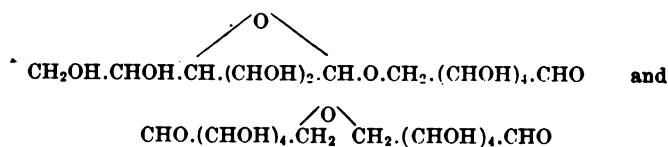
Sorbinose, also a ketohexose, occurs in the berries of the mountain ash. It does not ferment. Its osazone fuses at 164° .

DISACCHARIDS—SACCHAROBIOSES.

Disaccharids consist of two molecules of monosaccharids, united with elimination of H_2O . So far as is known they are all derived from the hexoses, and their formula is consequently $\text{C}_{12}\text{H}_{22}\text{O}_{11}$. They are all capable of yielding two hexose molecules by hydrolysis: $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} = 2\text{C}_6\text{H}_{12}\text{O}_6$, a change which is called "inversion." The union of the two monosaccharid molecules is either through the aldehyde, ketone, or alcoholic groups. Of the three most important disaccharids, saccharose, lactose and maltose, the first named has no reducing power, and yields no osazone with phenylhydrazin. It therefore contains no aldehyde or ketone group. When heated with acetic anhydrid to 160° it forms an octacetyl ester, $\text{C}_{12}\text{H}_{14}\text{O}_3(\text{O}.\text{C}_2\text{H}_3\text{O})_8$. It therefore contains eight hydroxyls. When hydrolyzed it yields d-glucose and d-fructose (laevogyatory). From the above facts we may infer that saccharose is derived from the two hexoses named, united through the aldehyde and ketone groups, a constitution which may be represented by the formulæ:



Lactose and maltose both cause reduction and yield osazones. On hydrolysis the former yields d-glucose and galactose, and the latter only d-glucose. They each consequently retain an aldehyde (or ketone) group, and their constitution may probably be represented thus:



The disaccharids are hydrolyzed by boiling with very dilute acids, or even with water, and by several enzymes such as diastase, emulsin, invertin, ptyalin, trypsin and pepsin.

Saccharose—Cane Sugar—exists in many roots, fruits and grasses, and is produced from the sugar-cane, *Saccharum officinarum*, sorghum, *Sorghum saccharatum*, beet, *Beta vulgaris*, and sugar-maple, *Acer saccharinum*.

For the extraction of sugar the expressed juice is heated in large pans to about 100° (212° F.); milk of lime is added, which causes

the precipitation of albumin, wax, calcic phosphate, etc.; the clear liquid is drawn off, and "delimed" by passing a current of CO_2 through it; the clear liquid is again drawn off and evaporated, during agitation, to the crystallizing point; the product is drained, leaving what is termed **raw** or **muscovado sugar**, while the liquor which drains off is **molasses**. The sugar so obtained is purified by the process of "refining," which consists essentially in adding to the raw sugar, in solution, albumen in some form, which is then coagulated; filtering first through canvas, afterward through animal charcoal; and evaporating the clear liquid in "vacuum-pans," at a temperature not exceeding 72° (161.6° F.), to the crystallizing point. The product is allowed to crystallize in earthen moulds; a saturated solution of pure sugar is poured upon the crystalline mass in order to displace the uncrystallizable sugar which still remains, and the loaf is finally dried in an oven. The liquid displaced as above is what is known as **sugar-house syrup**.

Pure sugar should be entirely soluble in water; the solution should not turn brown when warmed with dilute potassium hydroxid solution; should not reduce Fehling's solution, and should give no precipitate with ammonium oxalate.

Beet-sugar is the same as cane-sugar, except that, as usually met with in commerce, it is lighter, bulk for bulk. **Sugar-candy**, or **rock-candy**, is cane-sugar allowed to crystallize slowly from a concentrated solution, without agitation. **Maple-sugar** is a partially refined, but not decolorized variety of cane-sugar.

Saccharose crystallizes in small, white, monoclinic prisms; or, as sugar-candy, in large, yellowish, transparent crystals; sp. gr. 1,606. It is very soluble in water, dissolving in about one-third its weight of cold water, and more abundantly in hot water. It is insoluble in absolute alcohol or ether, and its solubility in water is progressively diminished by the addition of alcohol. Aqueous solutions of cane-sugar are dextrogyrous, $[\alpha]_D = +66.5^\circ$.

When saccharose is heated to 160° (320° F.) it fuses, and the liquid, on cooling, solidifies to a yellow, transparent, amorphous mass, known as **barley-sugar**; at a slightly higher temperature, it is decomposed into glucose and lævulosan; at a still higher temperature, H_2O is given off, and the glucose already formed is converted into glucosan; at about 200° (392° F.) the evolution of H_2O is more abundant, and there remains a brown material known as **caramel**, or **burnt sugar**; a tasteless substance, insoluble in strong alcohol, but soluble in H_2O , or in aqueous alcohol, and used to communicate color to spirits; finally, at higher temperatures, methyl hydrid and the two oxids of carbon are given off; a brown oil, acetone, acetic acid, and aldehyde distil over; and a carbonaceous residue remains.

If saccharose be boiled for some time with H_2O , it is converted into inverted sugar, which is a mixture of glucose and fructose: $C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$. With a solution of saccharose the polarization is dextrogyrous, but, after inversion, it becomes lævogyrous, because the left-handed action of the molecule of fructose produced, $[a]_D = -71.4^\circ$, is only partly neutralized by the right-handed action of the glucose, $[a]_D = +52.6^\circ$. This inversion of cane sugar is utilized in the testing of samples of sugar. On the other hand, it is to avoid its occurrence, and the consequent loss of sugar, that the vacuum-pan is used in refining—its object being to remove the H_2O at a low temperature.

With potassium chlorate, sugar forms a mixture which detonates when subjected to shock, and which deflagrates when moistened with H_2SO_4 . Concentrated H_2SO_4 blackens it. Dilute HNO_3 , when heated with saccharose, oxidizes it to saccharic and oxalic acids.

When moderately heated with liquor potassæ, cane-sugar does not turn brown, as does glucose; but by long ebullition it is decomposed by the alkalies, much less readily than glucose, with formation of acids of the fatty series and oxalic acid.

With the bases, saccharose forms definite compounds called **sucrates** (improperly saccharates, a name belonging to the salts of saccharic acid). With Ca it forms five compounds. Calcium hydroxid dissolves readily in solutions of sugar, with formation of a Ca compound, soluble in H_2O , containing an excess of sugar.

During the process of digestion, probably in the small intestine, cane-sugar is inverted.

Lactose—Milk Sugar—*Lactine*—*Saccharum lactis* (U. S., Br.)—occurs in the milk of the mammalia, in the amniotic fluid of cows, and in the urine of women towards the end of gestation and during lactation. It may be obtained from skim-milk by coagulating the casein with a small quantity of H_2SO_4 , filtering, evaporating, redissolving, decolorizing with animal charcoal, and recrystallizing.

It forms prismatic crystals; sp. gr. 1.53; hard, transparent, faintly sweet, soluble in 6 parts of cold and 2.5 parts of boiling H_2O ; soluble in acetic acid; insoluble in alcohol and in ether. Its solutions are dextrogyrous $[a]_D = +52.5^\circ$. The crystals, dried at 100° (212° F.), contain 1Aq, which they lose at 150° (302° F.).

Lactose is not altered by contact with air. Heated with dilute mineral acids or with strong organic acids, it is converted into galactose. HNO_3 oxidizes it to mucic and oxalic acids. A mixture of HNO_3 and H_2SO_4 converts it into an explosive nitro-compound. With organic acids it forms esters. With soda, potash and lime it forms compounds similar to those of saccharose, from which lactose may be recovered by neutralization, unless they have been heated to 100°

(212° F.), at which temperature they are decomposed. It reduces Fehling's solution, and reacts with Trommer's test. Its osazone fuses at 200° (392° F.).

In the presence of yeast, lactose is capable of alcoholic fermentation, which takes place slowly, and, as it appears, without previous transformation of the lactose into glucose and galactose. On contact with putrefying proteins it enters into lactic fermentation.

The average proportion of lactose in different milks is as follows: Cow, 5.5 per cent.; mare, 5.5; ass, 5.8; human, 5.3; sheep, 4.2; goat, 4.0. It is converted into galactose by the pancreatic secretion.

Maltose—is formed, along with dextrins, during the conversion of starch, or of glycogen, into sugar by the action of diastase (in malting grain), and of the enzymes of the saliva and the pancreatic juice. It is also an intermediate product in the hydrolysis of starch by dilute sulfuric acid. Maltose crystallizes in hard, white needles aggregated into crusts. It is less soluble in alcohol than is glucose, and has a much higher dextrogyratory power $[\alpha]_D = +137^\circ$. It reduces Fehling's solution. It is hydrolyzed by boiling with dilute acids, yielding only d-glucose. It is fermentable. Its osazone fuses as 206°. Nitric acid oxidizes it to d-saccharic acid.

Isomaltose—*Gallisin*—is formed along with maltose, in the action of diastase, saliva, or pancreatic juice, or of boiling dilute acids, on starch, and exists in beer and artificial glucose. It is also formed by the prolonged action of strong HCl on d-glucose. It is very soluble in water, very sweet, and does not ferment, or does so very slowly. Its osazone forms yellow needles, which fuse at 150° (302° F.), and are rather soluble in hot water.

TRISACCHARIDS.

Several members of this group have been obtained from different vegetables. They have the formula $C_{18}H_{32}O_{16}$. The best known are **Raffinose**, or **Melitose**, which occurs in eucalyptus-manna, in cotton seed, and in beet-sugar molasses; and **Melecitose**, from the manna of *Pinus larix*.

POLYSACCHARIDS.

The starches, gums, and celluloses, which form this class, have the empirical formula $C_6H_{10}O_5$, but their molecular weights are much greater than that represented by that formula. They are very widely distributed in vegetable nature. On hydrolysis they are finally decomposed to monosaccharids, for the most part hexoses, although some of the gums yield pentoses.

Starch—Amylum—the most important member of the group, exists in the roots, stems, and seeds of all plants; and is obtained commercially from rice, potatoes, and maize. It is a white powder, consisting of granules which are round, ovoid or irregular in outline, and, in some cases, marked with a central spot or line, called the **hilum**, and with concentric rings. Differences in the shape, size and markings of the granules are utilized to identify the vegetable from



FIG. 41. A, wheat-starch; B, oat-starch; C, maize-starch; D, potato-starch. $\times 300$ diameters.

which the starch was obtained. Some of the commoner forms are shown in Fig. 41. Air-dried starch contains 18% of water, of which it loses 8% in vacuo, and the remainder only at 145° (293° F.). Starch is insoluble in cold water and in alcohol. If 15 to 20 parts of H_2O be gradually heated with one part of starch, the granules swell at about 55° (131° F.), and at 80° (176° F.) they have lost their structure, have swelled to thirty times their original volume, and have formed a homogeneous, translucent, gelatinous mass, commonly known as **starch paste**. This hydrated starch consists of an

insoluble portion, **starch cellulose**, and a soluble portion, **granulose**, or **soluble starch**. Granulose forms an opalescent solution in water, from which it is precipitated as a white powder by alcohol. Its solutions are strongly dextrogyrous, $[\alpha]_D = +207^\circ$ (about). By prolonged boiling with water, or, more rapidly, by boiling dilute mineral acids, or by the action of diastatic enzymes, soluble starch is converted into dextrins, maltose, and finally, d-glucose. Dry heat causes the starch granules to burst, with formation of dextrin. A dilute solution of iodine produces a violet-blue color with starch, whether dry, hydrated, or in solution. The color is discharged by heat, but reappears on cooling. Concentrated HNO_3 dissolves starch in the cold, forming a nitro-product, called **xylochin**, or **pyroxam**, which is insoluble in water, soluble in a mixture of alcohol and ether, and explosive.

Glycogen—Animal Starch—occurs in the liver, the placenta, white blood corpuscles, pus cells, young cartilage cells, muscular tissue and many embryonic tissues, also in many molluscs. It is best obtained from liver tissue, by extraction with hot water and precipitation by alcohol, after separation of protein bodies by potassium iodohydrargyrate and acetic acid. It is a snow-white, floury powder, amorphous, tasteless, and odorless; soluble in water, forming an opalescent solution, insoluble in alcohol or ether. Its solutions are strongly dextrogyrous, $[\alpha]_D = +196.6^\circ$. Glycogen is converted into dextrins, maltose, and, ultimately, d-glucose by the action of boiling dilute acids, and by the salivary, pancreatic and hepatic diastatic enzymes. Glycogen is colored wine-red by iodine, the color being discharged by heat and returning on cooling. Its solutions dissolve, but do not reduce cupric hydroxide.

Other starches are: **Paramylum**, occurring in certain infusoria; **Lichenin**, in lichens and mosses; and **Inulin**, in the roots of dahlia, chicory and other plants.

Gums—are amorphous, translucent substances occurring in many plants. They are insoluble in alcohol and in ether. With water some of them, the **true gums**, form clear solutions; while others, the **vegetable mucilages**, swell up to sticky masses which cannot be filtered through paper. On boiling with dilute H_2SO_4 the gums yield d-glucose, galactose, or l-arabinose. Nitric acid oxidizes them to mucic, oxalic and saccharic acids.

The commoner members of the group are: **Arabin**, the chief constituent of gum arabic (acacia) and gum senegal; and **Bassorin**, the chief ingredient of gum tragacanth, Bassora gum, and plum and cherry gums.

Dextrin—British gum—a substance resembling gum arabic in appearance and in many properties, is obtained by one of three methods: (1) by subjecting starch to a dry heat of 175° (347°F.);

volume of H_2O , washing thoroughly, and drying. It is a tough material resembling animal parchment.

Gun-cotton—Pyroxylin—is obtained by dipping pure cotton in a cold mixture of one part of HNO_3 and two-thirds of H_2SO_4 for from three to ten minutes, washing thoroughly, and drying. It consists of hexanitrocellulose, $C_{12}H_{14}(O.NO_2)_6O_4$, is violently explosive, and is insoluble in a mixture of alcohol and ether.

Soluble pyroxylin—is obtained by acting on cotton with a warm mixture of twenty parts of nitre and thirty parts of concentrated H_2SO_4 , washing and drying. It consists of penta- and tetra-nitro-cellulose, is soluble in a mixture of alcohol and ether, and is used in the preparation of collodion. **Explosive gelatin, or smokeless powder**, is a desiccated mixture of nitro-glycerol and collodion. **Celluloid** is a mixture of gun-cotton and camphor, combined by pressure.

Tests for Carbohydrates.—A. *Furfurole Reactions*—dependent upon the formation of furfurole by the dehydrating action of concentrated H_2SO_4 upon carbohydrates (p. 509).

Molisch's Reaction.—To 1 cc. of the solution add two drops of a 15 per cent alcoholic solution of α -naphthol, and float the mixture upon concentrated H_2SO_4 . A deep violet band forms at the junction of the liquids. Addition of water produces a bluish violet ppt., soluble in the water. Addition of HNO_3 solution with a yellow color. Thymol may be used in place of α -naphthol. With the color is then carmine-red, turning at once to green on dilution. **Orcin's Reaction.**—To 1 cc. of the solution add two drops of a 15 per cent alcoholic solution of orcin, and float the mixture upon concentrated H_2SO_4 . A deep violet band forms at the junction of the liquids. Addition of water produces a bluish violet ppt., soluble in the water. Addition of HNO_3 solution with a yellow color. Thymol may be used in place of orcin. With the color is then carmine-red, turning at once to green on dilution.

Schiff's Reaction.—A paper moistened with a mixture of equal volumes of acetic acid and xylinum, with a little aniline, is placed over the mouth of the test-tube, and the liquid is poured into the test-tube. The paper is then heated with the solution. A blue color is produced. **Phloroglucin Reaction.**—To 1 cc. of the solution add two drops of a 15 per cent alcoholic solution of phloroglucin, and float the mixture upon concentrated H_2SO_4 . A deep violet band forms at the junction of the liquids. Addition of water produces a bluish violet ppt., soluble in the water. Addition of HNO_3 solution with a yellow color. Thymol may be used in place of phloroglucin. With the color is then carmine-red, turning at once to green on dilution. **Resorcin Reaction.**—To 1 cc. of the solution add two drops of a 15 per cent alcoholic solution of resorcin, and float the mixture upon concentrated H_2SO_4 . A deep violet band forms at the junction of the liquids. Addition of water produces a bluish violet ppt., soluble in the water. Addition of HNO_3 solution with a yellow color. Thymol may be used in place of resorcin. With the color is then carmine-red, turning at once to green on dilution.

B. Alcohol Reactions.—Dependent upon the presence of alcoholic hydroxyls in the carbohydrates. **Balmain's Reaction.**—Benzoyl

chlorid forms insoluble white ppts. of benzoyl esters in solutions of carbohydrates containing caustic soda. Similar insoluble benzoyl derivatives are formed by polyatomic alcohols and by diamins (p. 298).

C. Aldehyde and Ketone Reactions.—These reactions depend upon the presence in the carbohydrates of the CHO or CO group, and are consequently given by cane-sugar, non-reducing dextrins and starch, which do not contain such groups, only after their hydrolysis by boiling with dilute acids; but are given by other substances containing ketone or aldehyde groups.

1. *Copper Reduction Tests.*—These and other reduction tests are produced not only by aldoses and ketoses, but also by other reducing agents. Therefore, such substances, as well as albumin, must be excluded before these tests are resorted to. This may be accomplished by Focke's method, by boiling 10 cc. of the liquid (urine) with 5 cc. of CuSO_4 solution (1:10), filtering, adding 2 cc. Na_2CO_3 solution (1:10) to the cool filtrate, and filtering again after standing.

Trommer's Reaction is the earliest form of reduction test for sugar. It consists in adding about one-eighth of NaHO or KHO solution (1:10) to the dilute saccharine liquid, then two to three drops of CuSO_4 solution (1:10) and heating the blue liquid just to boiling. A yellow ppt. is formed, which becomes darker and reddish on boiling.

Fehling's Test.—The reagent must be kept in two solutions, which are to be mixed immediately before use. If the reagent be made in a single solution it is prone to self-reduction. Solution I consists of 34.653 gms. of crystallized CuSO_4 , dissolved in water to 500 cc.; and II, of 130 gms. of Rochelle salt dissolved to 500 cc. in NaHO solution of sp. gr. 1.12. When required for use equal volumes of the two solutions are mixed, and the mixture diluted with four volumes of water. A few cc. of this liquid are heated to boiling, and the saccharine liquid (urine) added in small portions, the contents of the test-tube being heated short of boiling, but not boiled, after each addition. A reducing sugar produces a yellow or red ppt., which forms more or less rapidly according to the amount of sugar present. The liquid should not be boiled after addition of urine, as creatinin and uric acid may reduce by boiling. Glucuronates and glycosurates also reduce. There are many modifications of this test, in which potassium tartrate, mannite, glycerol, etc., are used in place of Rochelle salt, but they present no advantages over the above. *Pavy's solution* is a modified Fehling, containing a notable amount of ammonia. It has the advantage for quantitative work (p. 751) that the blue color is more sharply discharged on total reduction, but it is open to the objection that the ppt. is soluble in the ammoniacal liquid.

Barfoed's Reaction is a modified Fehling, the reagent being a solution of 0.5 gm. of cupric acetate and 1 cc. of acetic acid in 100 cc. of

water. It is reduced by glucose in the cold and more rapidly on heating. It is not reduced by dextrins, saccharose or lactose, and serves to distinguish the last named sugar from glucose.

2. *Bismuth Reduction Tests*.—*Boettger's* test may be applied either in the manner originally indicated, or in *Nylander's* or *Almèn's* modifications. Equal portions of the liquid are placed in two test tubes, to each of which enough solution of Na_2CO_3 is added to make the reaction distinctly alkaline, and to one a little powdered bismuth subnitrate, and to the other a little powdered litharge are added. The contents of the two tubes are then heated to boiling, when, if the bismuth powder becomes black and the litharge remains unchanged, the presence of a reducing sugar may be inferred. The purpose of the litharge is to guard against error from the presence of sulfur compounds, which blacken both the bismuth and lead powders. *Nylander's solution* is made by adding 4 gms. of Rochelle salt, 2 gms. of bismuth subnitrate and 10 gms. of caustic soda to 90 cc. of water, boiling, cooling and filtering. To use the test 1 cc. of the reagent is added to the liquid and the mixture boiled, when a reducing sugar causes the formation of a gray or black ppt. A parallel testing with litharge is also required. An affirmative result is obtained with urine in the absence of sugar when large doses of quinin have been taken, but uric acid and creatinin do not react, and therefore this reaction is preferable to the copper reduction tests, although glucuronates react with it.

3. *Reduction of Other Metallic Compounds*.—Many other tests for aldoses and ketoses have been used, based upon the reduction of metallic salts other than those of copper and bismuth: auric chlorid, nickel sulfate, mercuric salts, molybdates, ferric salts, iodic acid, silver nitrate, lead salts and potassium dichromate. Of these the only one presenting any advantage over the copper and bismuth tests is Knapp's mercuric cyanid reaction, which gives a sharper end reaction, and is therefore preferable to the Fehling for quantitative determinations.

4. *Reduction of Organic Compounds*.—The *Mulder-Neubauer* test, based upon the reduction of indigo-blue; that of *Vogel*, in which litmus is substituted for indigo; the *Neumann-Wender* reaction, based upon the decolorization of methylene blue, and the reactions of *Baeyer*, *Quirini* and *Hoppe-Seyler*, based upon the reduction of orthonitropropionic acid to indigo are not preferable to the copper or bismuth reduction tests.

5. *Osazone Reaction*.—The *phenylhydrazin test*, or *Fischer's*, or *Riegler's test* depends upon the formation of osazones by all monosaccharids and disaccharids containing CO or CHO groups (p. 485). To 10 cc. of the liquid (urine) in a test tube, add 0.5 gm. phenylhydrazin hydrochlorid and 1 gm. sodium acetate, and cause the powders to dissolve by warming, and, if necessary, the addition of water, and

leave the test tube in a boiling-water bath for one hour, after which cool it by immersion in cold water. If a ketose or aldose, whether hexose or pentose, or a glucuronate be present a yellow ppt. is formed, usually crystalline, which should be collected and examined microscopically. Needle-shaped crystals are formed by glucose, fructose, maltose and glucuronic acid. The osazones of glucose and fructose are one and the same substance. The several osazones have different fusing points: that of glucuronic acid, 114° – 115° ; of isomaltose, 150° – 153° ; of arabinose, 159° ; of galactose, 193° ; of glucose and fructose, 204° – 205° , and of maltose, 206° . To determine the fusing point the ppt. is collected, dissolved in hot alcohol, the solution filtered and evaporated, the crystals dried over H_2SO_4 , placed in a small closed tube attached to the bulb of a thermometer by a pasted slip of paper, and heated in a paraffin bath, the temperature being noted when the material fuses. Aldehydes and ketones also form hydrazones.

6. *Villiers-Fayolle Reaction*.—This reaction and the following permit of the distinction between monaldoses and monoketoses. A solution of fuchsin which has been decolorized by sulfur dioxide (Schiff's reagent) is immediately turned red by aldehydes and by monaldoses, such as glucose (and invert sugar), and galactose, but not by ketones or monoketoses, such as fructose and sorbinose. The disaccharids, saccharose, maltose and lactose produce no color at first, but after a few days they become hydrolysed and the color appears, increasing in intensity.

7. *Seliwanoff's Reaction*, or *Conradi's reaction*, is given by ketohexoses, such as fructose and sorbinose, and by those disaccharids which yield ketoses on hydrolysis, as cane-sugar (and invert sugar), raffinose and inulin. The reaction consists in the formation of a red pigment, which is precipitated, and is soluble in alcohol with a red color, when the liquid is boiled with resorcinol and HCl .

8. *Berg's Reaction*.—Aldoses are oxidized by bromin to form acids which give an intense yellow coloration with very dilute and slightly acid Fe_2Cl_6 solution, but ketoses do not. From 0.2 to 0.3 gm. of the sugar, solid or in concentrated solution, is heated 10 minutes to 60° – 70° with 10 cc. of freshly prepared saturated bromin water, and then rapidly heated to the boiling point to expel excess of bromin. The colorless solution is tested with 10 cc. of a reagent made by adding to 100 cc. of water four drops of Fe_2Cl_6 solution, sp. gr. 1.45, and two drops of HCl , sp. gr. 1.17. Sugars containing no CHO give little or no color. Arabinose, glucose and galactose give strong reactions.

9. *Fermentation Test*.—Brewers' yeast and compressed yeast, which consist principally of *Saccharomyces cerevisiæ*, cause alcoholic fermentation of the d-hexoses easily, but do not ferment the l-hexoses or pentoses. And, as this yeast secretes invertin and maltase, it

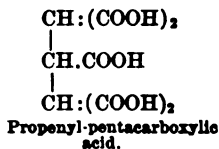
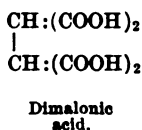
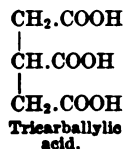
also causes alcoholic fermentation of saccharose and maltose immediately, and of lactose very slowly. The polyoses and glucosids only ferment after hydrolysis by boiling with dilute acids. Pure cultures of *S. apiculatus* and *S. membranæfaciens* secrete no invertin or maltase, and therefore do not ferment saccharose or maltose. For qualitative testing the evolution of gas under the influence of yeast is taken as evidence that fermentation has occurred. Three Smith's fermentation tubes are used, each containing a little compressed yeast, one filled with the liquid to be tested, the second with pure water, and the third with a dilute solution of glucose, and the three are put in a warm place over night. If gas collects in the first and third tubes, but not in the second, the liquid contains sugar; if gas collects in the third only it does not; under any other circumstances the yeast is at fault.

For methods of quantitative determination of glucose, see p. 750.

CARBOXYLIC ACIDS.

These compounds are the fourth products of oxidation of the paraffins (p. 283). and contain the characterizing group of atoms $O:C.OH$ (carboxyl). They are either pure acids, containing only the carboxyl and hydrocarbon groups; or alcohol-acids, containing also the groups CH_2OH , $CHOH$ or COH ; or aldehyde-acids, containing CHO ; or ketone-acids, containing CO ; or of still more complex function, containing two or more of the above groups.

The most important of the pure acids are those of the acetic ($C_nH_{2n}O_2$), and oxalic ($C_nH_{2n-2}O_4$) series, the former of which are monobasic, the latter dibasic. Other pure acids of higher basicity are also known in which the carboxyl groups are substituted for hydrogen atoms in the hydrocarbon. The following are examples of such acids:



PARAFFIN MONOCARBOXYLIC ACIDS—VOLATILE FATTY ACIDS—ACETIC SERIES—SERIES $C_nH_{2n}O_2$

The lowest terms of the series are volatile liquids, the highest are solids and exist in their glycerol esters in the fats; hence the name of **volatile fatty acids**. The solid acids, the tenth and higher of the series, cannot be distilled without decomposition except in superheated steam.

As the hydrocarbons may be considered as the hydrides of the alkyls (p. 274), and the alcohols as their hydroxids (p. 284), so the acids may be considered as the hydroxids of the **acidyls**: the acid or oxidized radicals. Thus acetic acid is acetyl hydroxid, $(\text{CH}_3.\text{CO})\text{OH}$.

These acids may be obtained:

(1) By oxidation of the corresponding alcohol or aldehyde: $\text{C}_2\text{H}_5.\text{CH}_2\text{OH} + \text{O}_2 = \text{C}_2\text{H}_5.\text{COOH} + \text{H}_2\text{O}$, or $2\text{CH}_3.\text{CHO} + \text{O}_2 = 2\text{CH}_3.\text{COOH}$; (2) By decomposition of the dicarboxylic acids (p. 334), with elimination of carbon dioxid: $\text{COOH}.\text{COOH} = \text{H}.\text{COOH} + \text{CO}_2$, and $\text{COOH}.\text{CH}_2.\text{COOH} = \text{CH}_3.\text{COOH} + \text{CO}_2$; (3) By the action of carbon monoxid upon an alkaline hydroxid or alcoholate: $\text{CO} + \text{NaHO} = \text{H}.\text{COONa}$, and $\text{CO} + \text{C}_2\text{H}_5.\text{O}.\text{Na} = \text{C}_2\text{H}_5.\text{COONa}$; (4) From the nitrils, or hydrocyanic esters (p. 393), by the action of acids or alkalies in the presence of water: $\text{HCN} + \text{H}_2\text{O} + \text{KHO} = \text{H}.\text{COOK} + \text{NH}_3$, or $\text{CH}_3.\text{CN} + 2\text{H}_2\text{O} + \text{HCl} = \text{CH}_3.\text{COOH} + \text{NH}_4\text{Cl}$. This constitutes a general method for the introduction of carboxyl, starting from the haloid derivatives of the hydrocarbon (p. 277). This is converted into the cyanid, or nitril (p. 393) by heating with alcoholic potassium cyanid: $\text{BrCH}_2.\text{CH}_3 + \text{KCN} = \text{CNCH}_2.\text{CH}_3 + \text{KBr}$, or $\text{BrCH}_2.\text{CH}_2\text{Br} + 2\text{KCN} = \text{CN}.\text{CH}_2.\text{CH}_2.\text{CN} + 2\text{KBr}$; and the cyanid is then converted into the acid by elimination of the nitrogen as ammonia, and the substitution of OOH in its place by the action of acids or of alkalies: $\text{CN}.\text{CH}_2.\text{CH}_3 + \text{HCl} + 2\text{H}_2\text{O} = \text{COOH}.\text{CH}_2.\text{CH}_3 + \text{NH}_4\text{Cl}$, or $\text{CN}.\text{CH}_2.\text{CH}_2.\text{CN} + 2\text{KHO} + 2\text{H}_2\text{O} = \text{COOK}.\text{CH}_2.\text{CH}_2.\text{COOK} + 2\text{NH}_3$ (pp. 335, 337, 428).

These acids form esters (p. 358) with alcohols, in the presence of HCl or H_2SO_4 , to absorb the water formed: $\text{CH}_3.\text{COOH} + \text{CH}_3.\text{CH}_2.\text{OH} = \text{CH}_3.\text{COO}(\text{C}_2\text{H}_5) + \text{H}_2\text{O}$. With halogens they form halid acids (p. 330): $\text{CH}_3.\text{COOH} + \text{Cl}_2 = \text{CH}_2\text{Cl}.\text{COOH} + \text{HCl}$. With phosphorus halids they form acidyl halids or anhydrids (p. 351): $\text{CH}_3.\text{COOH} + \text{PCl}_5 = \text{CH}_3.\text{CO}.\text{Cl} + \text{POCl}_3 + \text{HCl}$, and $2\text{CH}_3.\text{COOH} + \text{PCl}_5 = (\text{CH}_3\text{CO})_2\text{O} + \text{POCl}_3 + 2\text{HCl}$. Their ammonium salts, when heated, split off water to form amids (p. 400) and nitrils (p. 393): $\text{CH}_3.\text{COO}(\text{NH}_4) = \text{CH}_3.\text{CO}.\text{NH}_2 + \text{H}_2\text{O}$ and $\text{CH}_3.\text{COO}(\text{NH}_4) = \text{CH}_3.\text{CN} + 2\text{H}_2\text{O}$.

Formic Acid— $\text{H}.\text{COOH}$.—Although it is the first term of this series, formic acid differs from its superior homologues in several respects: (1) It is not a pure acid, but an aldehyde-acid, the single carbon atom forming part of both groups: $\text{O}:\text{C} \begin{smallmatrix} \text{OH} \\ \text{H} \end{smallmatrix}$; (2) The halogens do not convert it into halid-formic (or carbonic) acids, but split it to carbon dioxid and the hydracid: $\text{H}.\text{COOH} + \text{Cl}_2 = \text{CO}_2 + 2\text{HCl}$; (3) By elimination of water it yields carbon monoxid: $\text{H}.\text{COOH} = \text{CO} + \text{H}_2\text{O}$; (4) It produces no acidyl halid or anhydrid corresponding to those of its superior homologues.

It occurs in the bodies of ants and of other insects, and in the

blood, bile, perspiration and muscular fluid of mammalia. It is produced by oxidation of sugar, starch, gelatin, albumin, etc.; in the fermentation of diabetic urine; by the action of potash upon chloroform: $\text{CHCl}_3 + 4\text{KHO} = \text{H.COOK} + 3\text{KCl} + 2\text{H}_2\text{O}$; by the action of hydrating agents upon its nitril, hydrocyanic acid (p. 391): $\text{HCN} + 2\text{H}_2\text{O} = \text{H.COO}(\text{NH}_4)$; and by decomposition of oxalic acid in the presence of glycerol at about 100° : $\text{COOH.COOH} = \text{H.COOH} + \text{CO}_2$.

It is a colorless liquid of acid taste and penetrating odor, b. p. 100° , crystallizes at 0° , miscible with water. It is decomposed by mineral acids to carbon monoxid and water: $\text{H.COOH} = \text{CO} + \text{H}_2\text{O}$; by oxidizing agents to carbon dioxid and water: $2\text{H.COOH} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{CO}_2$; and by caustic alkalies to a carbonate and hydrogen: $\text{H.COOH} + \text{KHO} = \text{KHCO}_3 + \text{H}_2$. It reduces the salts of Au, Ag, and Hg.

Acetic Acid—*Acetyl Hydroxid*—*Acidum aceticum* (U. S., Br.)— $\text{CH}_3.\text{COOH}$ —is formed by the general methods, and (1) by the action of carbon dioxid on sodium methyl: $\text{CO}_2 + \text{NaCH}_3 = \text{CH}_3.\text{COONa}$; and (2) by the oxidation of many organic substances: starch, sugar, gelatin, fibrin, cellulose, tartaric and citric acids, etc. Commercially it is obtained as acetic acid and as vinegar. As the former it is produced by the dry distillation of wood, in which four products are obtained: charcoal, remaining in the retort, an illuminating gas, a tarry liquid, wood-tar, and an acid liquid, "crude wood vinegar" or "pyroxylic spirit." The last is a highly complex liquid, containing acids of this series, methyl acetate, and cyclic compounds. It is redistilled fractionally, the first portions being used as a source of methylic alcohol (p. 286), and the later portions of acetic acid. In these the acid is converted into sodium acetate, which, after calcination, is decomposed by H_2SO_4 , and the liberated acetic acid distilled off. The product so obtained, the commercial acid, contains 36 per cent of true acetic acid, sp. gr. 1.047.

Vinegar is obtained by the indirect atmospheric oxidation of various alcoholic liquids, containing less than 10 per cent of ethyl alcohol, under the influence of the growth of a true ferment, *Bacterium aceti*, or "mother of vinegar," with free access of air. It contains from 5 to 10 per cent of acetic acid.

Pure acetic acid, called **glacial acetic acid**, is obtained by distilling dry sodium acetate with a slight excess of H_2SO_4 . It is a colorless liquid, b. p. 119° , crystallizes to an ice-like mass at 17° , sp. gr. 1.0497 at 20° , having an acid taste and the odor of vinegar, and causing vesication when applied to the skin. Glacial acetic acid on dilution with water contracts until the sp. gr. becomes 1.0754 with a dilution of 77 per cent of acid, corresponding to a hydrate: $\text{CH}_3.\text{COOH} + \text{H}_2\text{O}$, and on further dilution the sp. gr. diminishes until at 50 per cent it is the same as that of the glacial acid. Acetic acid is a

good solvent for many organic substances, and is itself soluble in water and in alcohol in all proportions.

Vapor of acetic acid burns with a pale-blue flame and is decomposed at a red heat. Glacial acetic acid only decomposes calcium carbonate in the presence of water. Hot H_2SO_4 blackens and decomposes it, SO_2 and CO_2 being given off. Solutions of potassium acetate, when electrolyzed, yield ethane, C_2H_6 . Under ordinary circumstances chlorine acts upon acetic acid slowly, more actively under the influence of sunlight, to form the three products of substitution mentioned below.

Acetates are soluble in water, except basic ferric acetate. Potassium acetate, heated with arsenic trioxide, forms cacodyl oxide (p. 422). Calcium acetate, when heated alone, yields acetone (p. 307); and with calcium formate, aldehyde (p. 300).

Monochloroacetic acid is a solid, f. p. 62° , b. p. 186° , obtained, along with acetyl chloride, by the action of chlorine upon acetic anhydride: $(\text{CH}_3\text{CO})_2\text{O} + \text{Cl}_2 = \text{CH}_2\text{Cl.COOH} + \text{CH}_3\text{COCl}$. **Dichloroacetic acid** is a colorless liquid, b. p. 190° , obtained by heating chloral with aqueous potassium cyanide: $\text{CCl}_3\text{CHO} + \text{H}_2\text{O} + \text{KCN} = \text{CHCl}_2\text{COOH} + \text{KCl} + \text{HCN}$. **Trichloroacetic acid** is an odorless, strongly vesicant, crystalline solid, f. p. 46° , b. p. 195° , obtained by oxidation of chloral hydrate by nitric acid: $2\text{CCl}_3\text{CH(OH)}_2 + \text{O}_2 = 2\text{CCl}_3\text{COOH} + 2\text{H}_2\text{O}$. These three acids are extremely useful synthetic agents because of the facility with which the halogen is replaced by O, OH, NH_2 , etc. Thus by hydrolysis monochloroacetic acid yields glycollic acid: $\text{CH}_2\text{Cl.COOH} + \text{H}_2\text{O} = \text{CH}_2\text{OH.COOH} + \text{HCl}$; dichloroacetic acid yields glyoxylic acid: $\text{CHCl}_2\text{COOH} + \text{H}_2\text{O} = \text{CHO.COOH} + 2\text{HCl}$; and trichloroacetic acid yields oxalic acid: $\text{CCl}_3\text{COOH} + 2\text{H}_2\text{O} = \text{COOH.COOH} + 3\text{HCl}$. With ammonia monochloroacetic acid yields amidoacetic acid: $\text{CH}_2\text{Cl.COOH} + \text{NH}_3 = \text{CH}_2\text{NH}_2\text{COOH}$.

Mono-, di- and tribromo-, and iodoacetic acids are also known.

Superior Homologues of Acetic Acid.—Considering acetic acid as the first term of this series, by reason of the peculiarities of formic acid above referred to, the superior homologues may be considered as alkyl-acetic acids, which may be monoalkylic, as propionic, or methylacetic acid: $\text{CH}_3\text{CH}_2\text{COOH}$, dialkyllic, as isobutyric, or dimethylacetic acid: $(\text{CH}_3)_2\text{CH.COOH}$, or trialkylic, as pivalic, or trimethylacetic acid: $(\text{CH}_3)_3\text{C.COOH}$.

Propionic Acid—Methylacetic acid— $\text{CH}_3\text{CH}_2\text{COOH}$ —is formed by the action of caustic potash upon sugar, starch and gum; during acetic fermentation; in the distillation of wood; during the putrefaction of peas, beans, etc.; by the oxidation of normal propylic alcohol, etc. It is best prepared by heating ethyl cyanide with potash until the odor of the ester has disappeared; the acid is then liberated from its potassium compound by H_2SO_4 and purified.

It is a colorless liquid, sp. gr. 0.996, b. p. 140° , solidifies at -36.5° , odor and taste like those of acetic acid, mixes with water and alcohol. Its salts are crystalline and soluble.

While there exists only one of each monohalogen substitution product of acetic acid, there exist a greater number with the higher homologues, which differ with the position of the introduced halogen atom. Thus with propionic acid two are known: $\text{CH}_3.\text{CHCl}.\text{COOH}$, **alpha monochloropropionic acid**, and $\text{CH}_2\text{Cl}.\text{CH}_2.\text{COOH}$, **beta monochloropropionic acid** (p. 340). These acids are best obtained by the action of the hydracids upon lactic and hydraerylic acids respectively (pp. 341, 342): $\text{CH}_3.\text{CHOH}.\text{COOH} + \text{HBr} = \text{CH}_3.\text{CHBr}.\text{COOH} + \text{H}_2\text{O}$, and $\text{CH}_2\text{OH}.\text{CH}_2.\text{COOH} + \text{HCl} = \text{CH}_2\text{Cl}.\text{CH}_2.\text{COOH} + \text{H}_2\text{O}$. Because of the reducing power of HI (p. 99) β iodopropionic acid may also be obtained from glyceric acid (p. 342): $\text{CH}_2\text{OH}.\text{CHOH}.\text{COOH} + 3\text{HI} = \text{CH}_2\text{I}.\text{CH}_2.\text{COOH} + 2\text{H}_2\text{O} + \text{I}_2$. The β acids are also obtained by the action of hydracids upon the unsaturated acrylic acid: $\text{CH}_2:\text{CH}.\text{COOH} + \text{HI} = \text{CH}_2\text{I}.\text{CH}_2.\text{COOH}$. By the action of bromin upon propionic acid α monobromopropionic acid is formed, if the Br be not in excess, when the $\alpha\alpha$ dibromopropionic acid, $\text{CH}_3.\text{CBr}_2.\text{COOH}$ is formed. Lactic and hydraerylic acids are formed from the monohalid propionic acids by reactions the reverse of those given above. The β bromo- and iodo acids form adipic acid with finely divided silver: $2\text{CH}_2\text{Br}.\text{CH}_2.\text{COOH} + \text{Ag}_2 = \text{COOH}.\text{(CH}_2\text{)}_4.\text{COOH} + 2\text{AgBr}$. With ammonia they form amido propionic acid: $\text{CH}_2\text{Br}.\text{CH}_2.\text{COOH} + \text{NH}_3 = \text{CH}_2\text{NH}_2.\text{CH}_2.\text{COOH} + \text{HBr}$. Dihalid acids, $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$, with like or unlike halogens, are also known.

Butyric Acid—Ethylacetic Acid— $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{COOH}$ —exists in milk, perspiration, muscle, spleen, contents of stomach and large intestine, fæces, and guano; in butter, particularly when rancid; in certain fruits and in yeast. It is formed in the decomposition of many animal and vegetable substances, and particularly by *butyric fermentation* of carbohydrates in presence of proteins. This fermentation occurs in two stages: First lactic acid is produced from the carbohydrates: $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{C}_3\text{H}_6\text{O}_3$, and this is decomposed according to: $2\text{C}_3\text{H}_6\text{O}_3 = \text{C}_4\text{H}_8\text{O}_2 + 2\text{CO}_2 + 2\text{H}_2$.

Butyric acid is a colorless, mobile liquid, having a disagreeable, persistent odor of rancid butter, and a sharp, acid taste; soluble in water, alcohol, ether, and methyl alcohol; boils at 164° (327.2° F.), distilling unchanged; solidifies in a mixture of solid carbon dioxid and ether; sp. gr. 0.974 at 15° (59° F.); a good solvent of fats. It is not acted on by cold H_2SO_4 or HNO_3 . Hot HNO_3 oxidizes it to succinic acid: $2\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{COOH} + 3\text{O}_2 = 2\text{COOH}.\text{CH}_2.\text{CH}_2.\text{COOH} + 2\text{H}_2\text{O}$. Dry Cl in sunlight, and Br under heat and pressure form several products of substitution. The butyrates are soluble in water.

Butyric acid is formed in the intestine, by the process of fermentation mentioned above, at the expense of those portions of the carbohydrate elements of food which escape absorption, and is discharged with the fæces as ammonium butyrate.

Isobutyric Acid—Dimethylacetic acid— $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \text{CH} \cdot \text{COOH}$ —boils at 155° (311° F.), has been found in human fæces. It corresponds to isobutyl alcohol, from which it is produced by oxidation.

Valerianic Acids— $\text{C}_4\text{H}_9\text{COOH}$ —102.—Corresponding to the four primary amylic alcohols, there are four possible amylic or valerianic acids:

Normal Valerianic Acid—Propyl-acetic acid—Butyl-formic acid—is obtained by the oxidation of normal amylic alcohol. It is an oily liquid, boils at 185° (365° F.), and has an odor resembling that of butyric acid.

Ordinary Valerianic Acid—Isopropyl-acetic acid—Delphinic acid—Phoenic acid—Isovaleric acid—Isobutyl-formic acid—Acidum valerianicum (Br.).—This acid exists in the oil of the porpoise, and in valerian root and in angelica root. It is formed during putrid fermentation or oxidation of proteins. It occurs in the urine and fæces in typhoid, variola, and acute atrophy of the liver. It is also formed in a variety of chemical reactions, and notably by the oxidation of amylic alcohol.

The ordinary valerianic acid is an oily, colorless liquid, having an odor of old cheese, and a sharp, acid taste. It solidifies at -51° (-59.8° F.); boils at 173° – 175° (343.4° – 347° F.); sp. gr. 0.9343–0.9465 at 20° (68° F.); burns with a white, smoky flame. It dissolves in 30 parts of water, and in alcohol and ether in all proportions. It dissolves phosphorus, camphor and certain resins.

Methyl-ethyl-acetic Acid—boils at 175° (347° F.). It contains an asymmetric carbon atom and exists in two optically opposed modifications (p. 311).

Trimethyl-acetic Acid—Pivalic acid—is a crystalline solid, which fuses at 35.5° (96° F.) and boils at 163.7° (326.7° F.); sparingly soluble in H_2O ; obtained by the action of mercuric cyanid upon tertiary butyl iodid.

Caproic Acids—Hexylic acids— $\text{C}_5\text{H}_{11}\text{COOH}$ —116.—There exist seven isomeres having the composition indicated above, some of which have been prepared from butter, cocoa-oil and cheese, and by decomposition of amyl cyanid, or by oxidation of hexyl alcohol.

The acid obtained from butter, in which it exists as a glyceric ester, is a colorless, oily liquid, boils at 205° (401° F.); sp. gr. 0.931 at 15° (59° F.); has an odor of perspiration and a sharp, acid taste; is very sparingly soluble in water, but soluble in alcohol. It is the normal hexylic acid: $\text{CH}_3(\text{CH}_2)_4\text{COOH}$.

Enanthylic Acid—*Heptylic acid*— $C_6H_{13}.COOH$ —130—exists in spirits distilled from rice and maize, and is formed by the action of HNO_3 on fatty substances, especially castor-oil. It is a colorless oil; sp. gr. 0.9167; boils at 212° ($413.6^\circ F.$).

Caprylic Acid—*Octylic acid*— $C_7H_{15}.COOH$ —144—accompanies caproic acid in butter, cocoa-oil, etc. It is a solid; fuses at 15° ($59^\circ F.$); boils at 236° ($457^\circ F.$); almost insoluble in H_2O .

Pelargonic Acid—*Nonylic acid*— $C_8H_{17}.COOH$ —158.—A colorless oil, solid below 10° ($50^\circ F.$); boils at 260° ($500^\circ F.$); exists in oil of geranium, and is formed by the action of HNO_3 on oil of rue.

Capric Acid—*Decylic Acid*— $C_9H_{19}.COOH$ —172—exists in butter, cocoa-oil, etc., associated with caproic and caprylic acids in their glyceric esters, and in the residues of distillation of Scotch whisky, as amyl caprate. It is a white, crystalline solid; melts at 27.5° ($81.5^\circ F.$); boils at 273° ($523.4^\circ F.$).

Lauric Acid—*Laurostearic acid*— $C_{11}H_{23}.COOH$ —200—is a solid, fusible at 43.5° ($110.3^\circ F.$); obtained from laurel berries, cocoa-butter and other vegetable fats.

Myristic Acid— $C_{13}H_{27}.COOH$ —228.—A crystalline solid, fusible at 54° ($129.2^\circ F.$); existing in many vegetable oils, cow's butter and spermaceti.

Palmitic Acid—*Ethalic acid*— $C_{15}H_{31}.COOH$ —256—exists in palm-oil, in combination when the oil is fresh, and free when the oil is old; it also enters into the composition of nearly all animal and vegetable fats. It is obtained from the fats, palm-oil, etc., by saponification with caustic potash and subsequent decomposition of the soap by a strong acid. It is also formed by the action of caustic potash in fusion upon cetyl alcohol (ethal), and by the action of the same reagent upon oleic acid.

Palmitic acid is a white, crystalline solid; odorless, tasteless; lighter than H_2O , in which it is insoluble; quite soluble in alcohol and in ether; fuses at 62° ($143.6^\circ F.$); distils unchanged with vapor of water.

Margaric Acid— $C_{16}H_{33}.COOH$ —270—formerly supposed to exist as a glycerid in all fats, solid and liquid. What had been taken for margaric acid was a mixture of 90 per cent. of palmitic and 10 per cent. of stearic acid. It is obtained by the action of potassium hydroxid upon cetyl cyanid, as a white, crystalline body; fusible at 59.9° ($140^\circ F.$).

Stearic Acid— $C_{17}H_{35}.COOH$ —284—exists as a glycerid in all solid fats and in many oils, and also free to a limited extent.

To obtain it pure the fat is saponified with an alkali, and the soap decomposed by HCl ; the mixture of fatty acids is dissolved in a large quantity of alcohol, and the boiling solution *partly* precipitated by

the addition of concentrated solution of barium acetate. The precipitate is collected, washed and decomposed by HCl; the stearic acid which separates is washed and recrystallized from alcohol. The process is repeated until the product fuses at 70° (158° F.). Stearic acid is formed from oleic acid (p. 429) by the action of iodine under pressure at 270°–280° (518°–536° F.).

Pure stearic acid is a colorless, odorless, tasteless solid; fusible at 70° (158° F.); unctuous to the touch; insoluble in H₂O, very soluble in alcohol and in ether. The alkaline stearates are soluble in H₂O; those of Ca, Ba, and Pb are insoluble.

Stearic and palmitic acids exist free in the intestine during the digestive process, a portion of which is decomposed by the action of the pancreatic secretion into fatty acids and glycerol. The same decomposition also occurs in the presence of putrefying proteins.

Arachidic Acid— $\text{C}_{22}\text{H}_{42}\text{O}_4$ —exists as a glyceride in peanut oil, now largely used as a substitute for olive oil, in oil of ben, and in small quantity in butter. It is a crystalline solid, which melts at 75° (165° F.).

Myristic Acid— $\text{C}_{14}\text{H}_{28}\text{O}_4$ —exists in many vegetable oils, cow's butter and sperm oil.

PARAFFIN DICARBOXYLIC ACIDS—OXALIC SERIES— $\text{C}_2\text{H}_2\text{O}_4$ —exists in palm oil; the acids are derived from the oxidation of two ethylene groups and are distinguished by the number of methylene groups between the two carboxyl groups. They contain two carboxyl groups and are therefore dibasic. From the paraffin series the following acids are known: ethane dicarboxylic acid (oxalic acid), propane dicarboxylic acid (malonic acid), butane dicarboxylic acid (succinic acid), pentane dicarboxylic acid (glutaric acid), and from the five hexanes nine acids; all of which are lighter than H₂O, in which they are more soluble than in ether; fuses at 62° (143.6° F.); distils unchanged with vapor of water.

Margaric Acid— $\text{C}_{17}\text{H}_{32}\text{O}_4$ —formerly supposed to exist as a glyceride in the solid and liquid fats, but has been taken for margarine. It is a solid, colorless, odorless, and tasteless body, fusible at 53.9° (140° F.).

Stearic Acid— $\text{C}_{18}\text{H}_{34}\text{O}_4$ —exists as a glyceride in all the fats and oils. As the monocarboxylic acids may be considered as the hydroxyls of the acids (p. 328), corresponding to the alkyls of the monohydric alcohols (p. 284), so the dicarboxylic acids are the hydroxyls of the divalent acid radicals, which we will call *acidyls*, corresponding to the alkyls of the dihydric alcohols (p. 294).

The acids of this series may be obtained: (1) By the oxidation of the corresponding diprimary alcohols (p. 294), dialdehydes (p. 306), primary oxaldehydes (p. 308), primary oxyacids (p. 338), aldehyde acids (p. 346), paraffin monocarboxylic acids (p. 327), olefin monocarboxylic acids (p. 428) or paraffins (p. 282).

(2) By the reduction of the olefin dicarboxylic acids (p. 430).

(3) By the action of silver upon the monoiodo or monobromo ethyl acids: $2\text{BrCH}_2\text{COOH} + 2\text{Ag} \rightleftharpoons 2\text{AgBr} + \text{COOH.CH}_2\text{CH}_2\text{COOH}$.

when it is triturated dry with lead dioxide, is sufficiently active to

[illegible]

(2) When the two carboxylic acids obtained from neighboring carbon atoms the acids are decomposed into water and CO_2 . Although the constituents in these compounds are constant, the compounds are not identical. For example, $\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}(\text{COOH})_2$ are not identical. When the carboxylic acids are attached to remote carbon atoms their calcium salts are converted into a corrosive upon the addition of heat into acids, ketones, and carbonates. $\text{CH}_3\text{CH}_2\text{CO}_2\text{Ca}$ and $\text{CH}_3\text{CH}(\text{CO}_2\text{Ca})_2$ are not identical.

Oxalic Acid, $\text{COOH} \cdot \text{COOH}$ or $\text{C}_2\text{O}_4\text{H}_2$, 216-126 does not occur free in nature, but in the oxalates of K, Na, Ca, Mg, and Fe in the juices of many plants: sorrel, rhubarb, cichorium, oak, etc.; as a highly ferruginous oxalate in small quantity in human urine. It is prepared artificially by oxidizing sugar or starch by HNO_3 , or by the action of an alkaline hydroxid in fusion upon sawdust. The soluble alkaline oxalate obtained by the latter method is converted into the insoluble Ca or Pb salt which is washed and decomposed by an equivalent quantity of H_2SO_4 or H_3SbO_4 and the liberated acid purified by recrystallization.

an oxide acid is also formed by the oxidation of many organic substances, alcohol, glycol, sugar, etc.; by the action of potassium upon the alkali formates, and by the action of K or Na upon CO_2 . The metal itself is a monoxide as the acid itself.

It crystallizes in transparent prisms containing 2 Aq, which decompose on exposure to air, and lose their Aq slowly but completely at 100° (212°F.), or in a dry vacuum. It fuses at 98° (208.4°F.) in its Aq; at 110° – 132° (230° – 269.6°F.) it sublimes in the air.

drous form, while a portion is decomposed; above 160° (320° F.) the decomposition is more extensive; H_2O , CO_2 , CO , and formic acid are produced, while a portion of the acid is sublimed unchanged. It dissolves in 15.5 parts of water at 10° (50° F.); the presence of HNO_3 increases its solubility. It is quite soluble in alcohol. It has a sharp taste and an acid reaction in solution.

Oxalic acid is readily oxidized; in watery solution it is converted into CO_2 and H_2O , slowly by simple exposure to air, more rapidly in the presence of platinum-black or of the salts of platinum and gold, under the influence of sunlight, or when heated with HNO_3 , manganese dioxid, chromic acid, Br , Cl , or hypochlorous acid. Its oxidation, when it is triturated dry with lead dioxid, is sufficiently active to heat the mass to redness. H_2SO_4 , H_3PO_4 and other dehydrating agents decompose it into H_2O , CO and CO_2 .

Analytical Characters.—(1) In neutral or alkaline solution: a white ppt. with a solution of Ca salt. (2) Silver nitrate: a white ppt., soluble in HNO_3 , and in NH_4HO . The ppt. does not darken when the fluid is boiled, but when dried and heated on platinum foil, it explodes. (3) Lead acetate, in solutions not too dilute: a white ppt., soluble in HNO_3 , insoluble in acetic acid.

Toxicology.—Although certain oxalates are constant constituents of vegetable food and of the human body, the acid itself, as well as monopotassic oxalate, is a violent poison when taken internally, acting both locally as a corrosive upon the tissues with which it comes in contact and as a true poison, the predominance of either action depending upon the concentration of the solution. Dilute solutions may produce death without pain or vomiting, and after symptoms resembling those of narcotic poisoning. Death has followed a dose of 4 gm. of the solid acid, and recovery a dose of 30 gm. in solution. When death occurs, it may be almost instantaneously, usually within half an hour; sometimes after weeks or months, from secondary causes.

The treatment, which must be as expeditious as possible, consists in the administration, *first*, of lime or magnesia, or a soluble salt of Ca or Mg , suspended or dissolved in a *small* quantity of H_2O or mucilaginous fluid; afterward, if vomiting have not occurred spontaneously, and if the symptoms of corrosion have not been severe, an emetic may be given. The alkaline carbonates are of no value in cases of oxalic-acid poisoning, as the oxalates which they form are soluble and almost as poisonous as the acid itself. The ingestion of water, or the administration of warm water as an emetic, is contra-indicated when the poison has been taken in the solid form (or where doubt exists as to what form it was taken in), as they dissolve, and thus favor the absorption of the poison.

Malonic Acid— $\text{CH}_2\begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$ —is a product of the oxidation of malic acid (p. 344), or of normal propyl glycol. It is best obtained by the general method 4, p. 335. Monochloroacetic acid is converted into cyano-acetic acid by heating in alkaline solution with KCN: $\text{CH}_2\text{Cl.COOH} + \text{KCN} = \text{CN.CH}_2.\text{COOH} + \text{KCl}$. The cyano-acid is then hydrolysed by heating with KHO or HCl, thus: $\text{CN.CH}_2.\text{COOH} + 2\text{H}_2\text{O} = \text{COOH.CH}_2.\text{COOH} + \text{NH}_3$. It forms large prismatic crystals, soluble in water, alcohol and ether; fusible at 132° (269.6° F.), and decomposed at about 150° (302° F.) into acetic acid and carbon dioxid. Because of the position of the CH_2 group, between two CO groups, malonic acid is allied to the β ketonic acids (p. 347), and its esters undergo synthetic reactions similar to those of acetoacetic ester (p. 360).

Succinic Acid— $\begin{smallmatrix} \text{CH}_2-\text{COOH} \\ | \\ \text{CH}_2-\text{COOH} \end{smallmatrix}$ —118—exists in amber, coal, fossil wood, and in small quantity in animal and vegetable tissues. Its presence has been detected in the normal urine after the use of fruits and of asparagus, in the parenchymatous fluids of the spleen, thyroid, and thymus, and in the fluids of hydrocele and of hydatid cysts. It is also formed in small quantity during alcoholic fermentation; as a product of oxidation of many fats and fatty acids; and by synthesis from ethylene cyanid: $\text{CN}(\text{CH}_2)_2\text{CN} + 4\text{H}_2\text{O} = \text{COOH}(\text{CH}_2)_2\text{COOH} + 2\text{NH}_3$. It may also be obtained by dry distillation of amber, or by the fermentation of malic acid (p. 344).

It crystallizes in large prisms or hexagonal plates, which are colorless, odorless, permanent in air, acid in taste, soluble in water, sparingly so in ether and in cold alcohol. It fuses at 180° (356° F.), and distils with partial decomposition at 235° (455° F.). It withstands the action of oxidizing agents. Reducing agents convert it into the corresponding acid of the fatty series, butyric acid. With Br it forms products of substitution. H_2SO_4 is without action upon it. Phosphoric anhydrid removes H_2O and converts it into succinic anhydrid, $\text{C}_4\text{H}_4\text{O}_3$.

Isosuccinic Acid—*Methyl-malonic acid*— $\text{CH}_3.\text{CH}\begin{smallmatrix} \text{COOH} \\ \text{COOH} \end{smallmatrix}$ —is formed by the action of hydrating agents upon α cyanopropionic acid. It forms prismatic crystals, fusible at 130° (266° F.), and is decomposed at higher temperatures into propionic acid and carbon dioxid.

Glutaric Acid— $\text{COOH}(\text{CH}_2)_3\text{COOH}$ —*Normal Pyrotartaric acid*—the next superior homologue of succinic acid, is formed by reduction of α oxyglutaric acid (p. 344). It crystallizes in large plates, very soluble in water, which fuse at 27° (206.4° F.). The corresponding amido-acid is one of the products of decomposition of protein bodies.

The **pyrotartaric acid** obtained by the action of heat on tartaric acid is **methyl-succinic acid**, $\text{COOH}.\text{CH}(\text{CH}_3).\text{CH}_2.\text{COOH}$, which may also be produced synthetically by the action of nascent H upon itaconic acid, $\text{COOH}.\text{C}(:\text{CH}_2).\text{CH}_2.\text{COOH}$, as well as by other methods. It fuses at 112° (233.6°F.), and forms rhombic prisms, very soluble in water, alcohol, and ether.

Adipic Acid— $\text{COOH}(\text{CH}_2)_4.\text{COOH}$ —is a product of the action of nitric acid on fats: **Pimelic acid**, $\text{COOH}(\text{CH}_2)_5.\text{COOH}$, and **Suberic acid**, $\text{COOH}(\text{CH}_2)_6.\text{COOH}$ —are similarly obtained from cork. **Azelaic acid**, $\text{C}_9\text{H}_{18}\text{O}_4$, **Sebacic acid**, $\text{C}_{10}\text{H}_{18}\text{O}_4$, **Brassylic acid**, $\text{C}_{11}\text{H}_{20}\text{O}_4$, and **Rocellic acid**, $\text{C}_{17}\text{H}_{32}\text{O}_4$, also belong to this series.

PARAFFIN TRI-, TETRA-, AND PENTA-CARBOXYLIC ACIDS.

Tricarboxylic Acids in which more than one carboxyl are attached to the same carbon atom exist only in their esters. The simplest of these: **Methenyl tricarboxylic ester**, $\text{CH}(\text{COO}.\text{C}_2\text{H}_5)_3$, is a crystalline solid, fusing at 29° (84.2°F.), and boiling at 253° (487.4°F.).

Tricarballic Acid— $\text{CH}_2(\text{COOH}).\text{CH}(\text{COOH}).\text{CH}_2(\text{COOH})$ —in which the carboxyls are attached to different carbon atoms, is a more stable compound. It exists in unripe beets and in the vacuum pan residues of beet-sugar works. It is formed by a variety of reactions, as by heating tribromhydrin with potassium cyanid and decomposing the cyanid with potash: $\text{CH}_2\text{Br}.\text{CHBr}.\text{CH}_2\text{Br} + 3\text{KCN} = \text{CH}_2\text{CN}.\text{CHCN}.\text{CH}_2\text{CN} + 3\text{KBr}$, and $\text{CH}_2\text{CN}.\text{CHCN}.\text{CH}_2\text{CN} + 6\text{H}_2\text{O} = \text{CH}_2\text{COOH}.\text{CH}(\text{COOH}).\text{CH}_2\text{COOH} + 3\text{NH}_3$. It forms rhombic prisms soluble in water, fusible at 164° (327.2°F.).

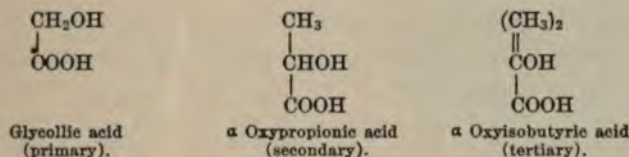
Camphoronic Acid— $\alpha\beta$ trimethyl-tricarballic acid— $(\text{CH}_3)_2\text{C}(\text{COOH}).(\text{CH}_3)\text{C}(\text{COOH}).\text{CH}_2(\text{COOH})$ —is a product of oxidation of camphor (q. v.).

Dimalonic Acid— $\begin{matrix} \text{COOH} \\ \diagup \end{matrix} \text{CH}.\text{CH} \begin{matrix} \diagdown \\ \text{COOH} \end{matrix}$ —the simplest of the tetracarboxylic acids, is a crystalline solid, fusible at 168° (334.4°F.). On further heating it yields ethylene succinic acid: $(\text{COOH})_2\text{CH}.\text{CH}(\text{COOH})_2 = \text{COOH}.\text{CH}_2.\text{CH}_2.\text{COOH} + 2\text{CO}_2$.

Propenyl-pentacarboxylic acid— $\text{C}_3\text{H}_3(\text{COOH})_5$ —is also known.

ALCOHOL-ACIDS—OXYACIDS.

These acids contain, besides the carboxyl group, one of the groups CH_2OH , CHOH , or COH , which characterize the primary, secondary, and tertiary alcohols. They, therefore, have the function of alcohols, primary, secondary, or tertiary, as well as that of acids:



They may be considered as derived either from the di- and polyatomic alcohols (glycols, glycerols, etc.) by incomplete oxidation, as $\text{COOH}.\text{CH}_2\text{OH}$ from $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$; or from the pure acids by substitution of OH for H atoms in the remaining hydrocarbon groups, as $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2.\text{COOH}$; $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2.\text{COOH}$, and $\text{CH}_2\text{OH}.\text{CHOH}.\text{CHOH}.\text{COOH}$ from $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{COOH}$.

The *basicity* of these acids is represented by the number of carboxyl groups which they contain, their *atomicity* by the number of hydroxyls. Thus $\text{CH}_2\text{OH}.\text{CHOH}.\text{COOH}$ is monobasic and triatomic.

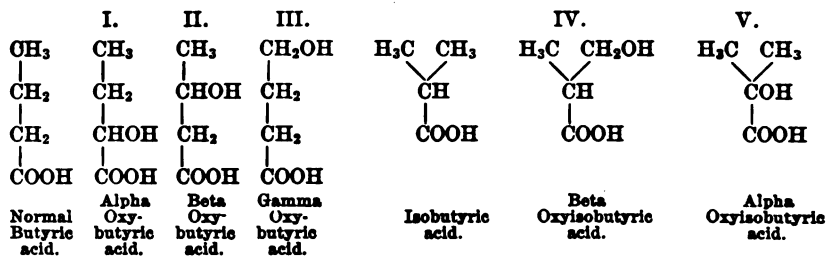
The algebraic formulæ of the several monobasic series are $\text{C}_n\text{H}_{2n}\text{O}_3$; $\text{C}_n\text{H}_{2n}\text{O}_4$, $\text{C}_n\text{H}_{2n}\text{O}_5$, etc., those of the dibasic series $\text{C}_n\text{H}_{2n-2}\text{O}_5$, $\text{C}_n\text{H}_{2n-2}\text{O}_6$, etc.; and those of the tribasic series $\text{C}_n\text{H}_{2n-4}\text{O}_7$, $\text{C}_n\text{H}_{2n-4}\text{O}_8$, etc.

OXYACETIC SERIES. $\text{C}_n\text{H}_{2n}\text{O}_3$.

The acids of this series contain one carboxyl and one alcoholic group. They are, therefore, monobasic and diatomic, and may be considered as derived from the glycols by oxidation of one CH_2OH group, or from the acids of the acetic series by substitution of OH for H in a hydrocarbon group (oxyacetic).

They are formed: (1) By the limited oxidation of the corresponding glycols or oxyaldehydes: $\text{CH}_2\text{OH}.\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{OH}.\text{COOH} + \text{H}_2\text{O}$, or, $2\text{CH}_2\text{OH}.\text{CHO} + \text{O}_2 = 2\text{CH}_2\text{OH}.\text{COOH}$; (2) By the action of nascent hydrogen upon the aldehyde or ketone acids (p. 346), or upon the acids of the oxalic series: $\text{CHO}.\text{COOH} + \text{H}_2 = \text{CH}_2\text{OH}.\text{COOH}$, or, $\text{CH}_3.\text{CO}.\text{COOH} + \text{H}_2 = \text{CH}_3.\text{CHOH}.\text{COOH}$, or, $\text{COOH}.\text{COOH} + 2\text{H}_2 = \text{CH}_2\text{OH}.\text{COOH} + \text{H}_2\text{O}$; (3) By heating the monohalogen fatty acids with silver or potassium hydroxids, or with water: $\text{CH}_2\text{Cl}.\text{COOH} + \text{KHO} = \text{CH}_2\text{OH}.\text{COOH} + \text{KCl}$, or, $\text{CH}_2\text{Cl}.\text{COOH} + \text{H}_2\text{O} = \text{HCl} + \text{CH}_2\text{OH}.\text{COOH}$; (4) From the aldehydes and ketones, by their conversion, first into oxycyanids by the action of hydrocyanic acid: $\text{CH}_3.\text{CHO} + \text{HCN} = \text{CH}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$, and the action upon these of acids or alkalis: $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix} + 2\text{H}_2\text{O} = \text{CH}_3.\text{CHOH}.\text{COOH} + \text{NH}_3$.

Isomeres—Position or Place Isomery.—Considering the oxybutyric acids as derived from normal and isobutyric acids by substitution of one OH for a hydrogen atom in a hydrocarbon group, the following five derivatives are possible:



While III, IV, and V are obviously different in molecular structure from each other and from I and II, in that the latter contain the group CHOH, while the former contain the groups CH₂OH, CH, and COH, the only difference between I and II, whose molecules are composed of identical groups, is in the *position* or *place* of the alcoholic hydroxyl with reference to the carboxyl group. Place isomers of this kind are distinguished by designating that in which the second substituted group (in this case the OH) is attached to the carbon atom contiguous to the first as the alpha, or 1-compound, and the others by the succeeding Greek letters, or by the numerals in the order of the removal of the position of the second substitution. Thus II above is Beta oxybutyric or 2-oxybutyric acid. (See Orientation, p. 436.)

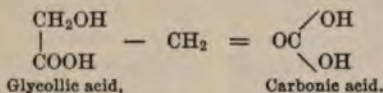
The α , β , γ , and δ acids differ in their products of dehydration: The α acids yields cyclic double esters, called **lactids**, by elimination of H₂O from two molecules of the acid (p. 368). The β acids are converted into unsaturated acids by loss of H₂O from one molecule of the acid: CH₂OH.CH₂.COOH = CH₂:CH.COOH + H₂O. The γ and δ acids, and those of greater carbon content, are converted into simple cyclic esters, called **lactones**, by elimination of H₂O from a single molecule of the acid (p. 368).

By further oxidation the primary oxyacids containing CH₂OH yield aldehyde acids: 2CH₂OH.COOH + O₂ = 2CHO.COOH + 2H₂O, and then dibasic acids: 2CHO.COOH + O₂ = 2COOH.COOH; the secondary acids, containing CHOH, yield ketone acids: 2CH₃.CHOH.COOH + O₂ = 2CH₃.CO.COOH + 2H₂O, and the tertiary acids, containing COH, yield ketones, carbon dioxide and water: 2 $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} > \text{COH} \cdot \text{COOH} + \text{O}_2 = 2\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 + 2\text{CO}_2 + 2\text{H}_2\text{O}$.

The hydrogen of their carboxyl group may be replaced to form salts, esters, or amids; and the hydroxyl of their alcoholic group may be replaced by alkali metals, alkyls, or acyls. In other words, they behave as acids and as alcohols.

Oxyformic Acid—Carbonic acid—OC(OH)₂.—Although this acid does not exist free, but is decomposed as soon as liberated into CO₂ and H₂O (p. 269), its salts, the carbonates, are well known and quite

stable. The position of this acid in this series is an apparent anomaly, as it is dibasic, not monobasic like the other terms of the series. But if we bear in mind that the basic nature of the H atom in a hydroxyl depends upon its close union with a CO group (or some other electro negative group), it is evident that the two H atoms in the inferior homologue of glycollic acid, being similarly united to the same CO group, must be equally basic :



Indeed, carbonic acid is not an alcohol acid, but a pure acid, as it contains no alcoholic group.

Esters are also known corresponding to **orthocarbonic acid**: $\text{C}(\text{OH})_4$, although the acid itself is unknown.

Glycollic Acid—Oxyacetic acid— $\text{CH}_2\text{OH}.\text{COOH}$ —is formed by the oxidation of glycol, by the action of nitrous acid upon glyecoll, and by the action of KHO upon monochloracetic acid, or upon **glyoxal**, $\text{CHO}.\text{CHO}$.

It forms deliquescent acicular crystals, very soluble in water, alcohol and ether. It fuses at 80° (176°F.). It is oxidized by HNO_3 to oxalic acid.

Lactic Acids—Oxypropionic acids—Alpha oxypropionic acid—Ethidene lactic acid— $\text{CH}_3.\text{CHOH}.\text{COOH}$ —is formed from milk sugar, cane sugar, gum and starch by *lactic fermentation*, induced by the lactic acid bacillus. It consequently exists in many soured products, such as soured milk, sour-kROUT, fermented beet-juice, and the waste liquors of starch works and of tanneries. It is formed in the stomach during digestion of carbohydrates. It is prepared by allowing a mixture of cane sugar, tartaric acid, rotten cheese, skim milk and chalk to ferment for ten days at 35° (95°F.). It has also been obtained by oxidation of alpha propylene glycol: $\text{CH}_3.\text{CHOH}.\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_3.\text{CHOH}.\text{COOH} + \text{H}_2\text{O}$.

Lactic acid of fermentation is a colorless, or yellowish, syrupy liquid; sp. gr. 1.215 at 20° (68°F.); soluble in water, alcohol and ether. It does not distil without decomposition, but when heated it yields lactid (p. 368), carbon monoxid, aldehyde and water. Oxidizing agents convert it into pyrroacemic acid: $\text{CH}_3.\text{CO}.\text{COOH}$; or, if more energetic, split it up into acetic acid and carbon dioxide: $\text{CH}_3.\text{CHOH}.\text{COOH} + \text{O}_2 = \text{CH}_3.\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$. Heated to 130° (266°F.) with dilute sulfuric acid it splits into aldehyde and formic acid: $\text{CH}_3.\text{CHOH}.\text{COOH} = \text{CH}_3.\text{CHO} + \text{H}.\text{COOH}$. Hydriodic acid reduces it to propionic acid; but hydrobromic acid converts it into α -bromopropionic acid.

Ethidene lactic acid contains an asymmetric carbon atom (p. 312): $\text{CH}_3\text{C}^*\text{HOH.COOH}$; and that produced by lactic fermentation is optically inactive ($d+1$). The **dextro acid**, also known as **sarcosolactic** or **paralactic acid**, is best obtained from Liebig's meat extract; and is also produced by allowing *Penicillium glaucum* to grow in a solution of inactive ammonium lactate. It exists in muscular tissue after death and during contraction, and in the spleen, lymphatic glands, thymus, thyroid, blood, bile, transudates, in the perspiration in puerperal fever, and in the urine after violent exercise, in yellow atrophy of the liver and in phosphorus poisoning, either free or in combination. The acid in muscular tissue probably originates from glycogen.

Laevolactic Acid is formed by the growth of *Bacillus acidi laevolactici* in a solution of cane sugar.

Ethylene Lactic Acid—Beta oxypropionic acid—Hydracrylic acid— $\text{CH}_2\text{OH.CH}_2\text{COOH}$ —the third form of lactic acid, is formed by the action of moist silver oxid upon β -iodo- or β -chloropropionic acid; by the saponification of ethylene cyanhydrin; or by the oxidation of the corresponding glycol. It is a thick, uncrystallizable syrup, which is converted by dehydration into acrylic acid $\text{CH}_2\text{OH.CH}_2\text{COOH}=\text{CH}_2:\text{CH.COOH}+\text{H}_2\text{O}$. On oxidation it yields oxalic acid and carbon dioxid: $2(\text{CH}_2\text{OH.CH}_2\text{COOH})+5\text{O}_2=2(\text{COOH.COOH})+2\text{CO}_2+4\text{H}_2\text{O}$.

Oxybutyric Acids.—Five isomeres are possible (p. 340). **Beta oxybutyric acid**— $\text{CH}_3\text{C}^*\text{HOH.CH}_2\text{COOH}$, is formed by the action of sodium amalgam upon acetoacetic ester (p. 360) $\text{CH}_3\text{CO.CH}_2\text{COOH}+\text{H}_2=\text{CH}_3\text{CHOH.CH}_2\text{COOH}$. The *laevo*-acid, a colorless syrup, readily soluble in water, alcohol and ether, occurs, accompanied by acetoacetic acid, in the blood and urine in severe cases of diabetes.

Alpha Oxycaproic Acid— $\text{CH}_3\text{.(CH}_2)_3\text{CHOH.COOH}$ —is **leucic acid**, obtained by oxidizing leucin (p. 414) by nitrous acid.

HIGHER MONOCARBOXYLIC OXYACIDS.

Representatives of the following series are known:

Dioxymonocarboxylic Series, Glyceric Series— $\text{C}_n\text{H}_{2n}\text{O}_4$.—The acids of this series bear the same relation to the glycerols that those of the oxyacetic series bear to the glycols. **Glyceric acid**, $\text{CH}_2\text{OH.C}^*\text{HOH.COOH}$, is an uncrystallizable syrup obtained by the limited oxidation of glycerol.

Trioxymonocarboxylic Series— $\text{C}_n\text{H}_{2n}\text{O}_5$ —of which **erythritic**, or **erythroglucic acid**: $\text{CH}_2\text{OH.(CHOH)}_2\text{COOH}$, derived from erythrol (p. 297) is the first term.

Tetroxymonocarboxylic Series— $C_nH_{2n}O_6$ —are obtained by oxidation of the aldopentoses (p. 310).

Pentoxymonocarboxylic Series— $C_nH_{2n}O_7$ —are obtained by oxidation of the hexahydric alcohols and aldohexoses. Synthetically, they are produced from the aldopentoses, by their conversion into nitrils of the oxyacids by CNH, and the action upon these of HCl, thus 1-arabinose $CH_2OH.(CHOH)_3.CHO$ yields 1-glucononitril, $CH_2OH.(CHOH)_3.CH(OH)CN$, and this yields 1-gluconic acid, $CH_2OH.(CHOH)_4.COOH$.

These acids are very unstable when free, easily losing water to form lactones (p. 368). They readily unite with phenylhydrazin to form phenylhydrazids, such as gluconophenyl hydrazid: $CH_2OH.(CHOH)_4.CO.NH.NH.C_6H_5$, which crystallize in characteristic forms (pp. 311, 485). They form numerous space isomeres. Their lactones treated with sodium amalgam, take up H_2 and produce the corresponding aldohexoses: thus gluconolactone yields glucose.

Mannonic Acids— $C_5H_6(OH)_5.COOH$.—The three acids, d-, l-, and (d+l), derived from the corresponding mannitols, yield the corresponding dibasic mannosaccharic acids on oxidation. They are syrupy liquids, which are converted into their lactones by evaporation of their solutions. On heating d- and l-mannonic acids with quinolin to 140° ($284^\circ F.$), they are, in part, converted into d- and l-gluconic acids. By this action and the subsequent conversion of gluconolactone, referred to above, glucose may be synthetically obtained from mannitol.

Gluconic Acids— $CH_2OH.(CHOH)_4.COOH$.—The d-, l-, and (d+l) acids are known. By oxidation they yield the corresponding saccharic acids. The lactones yield d-, l-, and (d+l) glucose by reduction. *d-Gluconic acid*, also known as **dextronic** or **maltonic acid**, is a syrup which forms a crystalline lactone on evaporation of its solution. It is formed by oxidizing dextrose, dextrin, starch, cane sugar, or maltose by chlorin or bromin water.

Acids belonging to the still higher series $C_nH_{2n}O_8$, $C_nH_{2n}O_9$, and $C_nH_{2n}O_{10}$, corresponding to the heptoses, octoses and nonoses (p. 309) are also known.

MONOXYDICARBOXYLIC SERIES— $C_nH_{2n-2}O_5$.

The acids of this series contain two carboxyls and one alcoholic group. They are, therefore, dibasic and triatomic, and may be considered as derived from the glycerols by oxidation of both CH_2OH groups. They may also be considered as derived from the paraffin dicarboxylic acids (oxalic series), above the first, by substitution of OH for H in a hydrocarbon group, in the same manner as the acids

of the oxyacetic series are derived from those of the acetic series (p. 339).

Tartronic Acid—Oxymalonic acid— $\text{COOH}.\text{CHOH}.\text{COOH}$ —is formed by the action of moist silver oxid upon monochloro- or monobromo-malonic acid, or by oxidation of glycerol by potassium permanganate. It crystallizes in large prisms, readily soluble in water, alcohol, and ether, and fusible at 184° (363.2°F.).

Malic Acid—Oxysuccinic acid— $\text{COOH}.\text{CH}_2.\text{C}^*\text{HOH}.\text{COOH}$ —exists in three modifications. The lævo-acid exists free, and in combination with K, Na, Ca, Mg, and organic bases in apples, pears, and similar fruits, and in the berries of the mountain ash and in gooseberries. The inactive ($d+l$), acid may be obtained from monobromo-succinic acid by the action either of moist silver oxid, of dilute HCl, of dilute NaHO, or even of boiling water; and by several other methods. The dextro-acid is obtained by the reduction of dextro-tartaric acid by hydriodic acid.

The natural malic acid crystallizes in prismatic needles; odorless; acid in taste; fusible at 100° (212°F.); deliquescent; very soluble in water and in alcohol. Heated to 140° (284°F.) it loses water with formation of fumaric acid, $\text{COOH}.\text{CH}:\text{CH}.\text{COOH}$. At 180° (356°F.) it yields water, fumaric acid and maleic anhydrid, $\begin{array}{c} \text{CH.CO} \backslash \\ \parallel \\ \text{CH.CO} / \text{O} \end{array}$.

Reducing agents convert it into succinic acid. The malates are oxidized to carbonates in the body.

Oxyglutaric Acid exists in the two isomeres: α oxyglutaric acid, $\text{COOH}.\text{CH}(\text{OH}).\text{CH}_2.\text{CH}_2.\text{COOH}$, which occurs in molasses, crystallizes with difficulty, and fuses at 72° (161.6°F.); and β oxyglutaric acid, $\text{COOH}.\text{CH}_2.\text{CHOH}.\text{CH}_2.\text{COOH}$, which fuses at 95° (203°F.).

DIOXYDICARBOXYLIC ACIDS— $\text{C}_4\text{H}_6\text{O}_6$.

Tartaric Acids—Dioxyethylene Succinic Acids.—There exist four acids having the composition $\text{C}_4\text{H}_6\text{O}_6$, which are readily convertible one into the other. They are: *Dextro-tartaric*, or *ordinary tartaric acid*; *lævo-tartaric acid*; *mesotartaric*, or *antitartaric acid*; and *racemic*, or *paratartaric acid*. The first three of these are stereoisomeres, due to the presence of two asymmetric carbon atoms in the molecule, whose molecular structure has been discussed under the head of space isomery (p. 312). Mesotartaric acid, which is optically inactive, has a molecular structure differing from those of the d - and l -acids, into which it cannot be split. Racemic acid, also optically inactive, is the ($d+l$) acid, and can be readily decomposed into them or separated from a mixture of them.

Dextro-tartaric Acid—Ordinary tartaric acid—Acidum tartaricum

(U. S.; Br.)—occurs, both free and in combination, in the sap of the vine and in many other vegetable juices and fruits, particularly in grape-juice. Although this is probably the only tartaric acid existing in nature, all four varieties may occur in the commercial acid, being formed during the process of manufacture. Tartaric acid is obtained in the arts from hydropotassic tartrate, or cream of tartar (p. 290).

The ordinary tartaric acid crystallizes in large prisms; very soluble in H_2O and in alcohol; acid in taste and reaction. Heated with water at 165° – 175° (329° – 347° F.) it is converted into mesotartaric and racemic acids. It fuses at 170° (338° F.); at 180° (356° F.) it loses H_2O , and is gradually converted into an anhydrid; at 200° – 210° (392° – 410° F.) it is decomposed with formation of pyruvic acid, $C_3H_4O_3$ (p. 347), and pyrotartaric acid, $C_5H_8O_4$, (p. 338); at higher temperatures CO_2 , CO , H_2O , hydrocarbons and charcoal are produced.

Tartaric acid is attacked by oxidizing agents with formation of CO_2 , H_2O , and, in some instances, formic and oxalic acids. Certain reducing agents convert it into malic and succinic acids. With fuming HNO_3 it forms a dinitro-compound, which is very unstable, and which, when decomposed below 36° (96.8° F.), yields tartaric acid. It forms a precipitate with lime-water, soluble in an excess of H_2O . In not too dilute solution it forms a precipitate with potassium sulfate solution. It does not precipitate with the salts of Ca. When heated with a solution of auric chlorid it precipitates the gold in the metallic form.

When taken into the economy, as it frequently is in the form of tartrates, the greater part is oxidized to carbonic acid (carbonates); but, if taken in sufficient quantity, a portion is excreted unchanged in the urine and perspiration. The free acid is poisonous in large doses. The acids and its salts are largely used in pharmacy and in dyeing.

Lævo-tartaric—forms crystals similar to those of the dextro acid, but having opposite hemihedral facets (p. 16), so that the crystals of one acid resemble the reflection of those of the other in a mirror.

Racemic Acid—(*d+l*) *Tartaric acid*—is produced when concentrated solutions of equal quantities of *d*- and *l*-tartaric acids are mixed. It is formed by oxidation of dulcitol and of mannitol. It is obtained by the action of moist silver oxid upon dibromo succinic acid: $COOH.CHBr.CHBr.COOH + 2AgHO = COOH.CHOH.CHOH.COOH + 2AgBr$; and by several other synthetic methods. It crystallizes in rhombic prisms, less soluble in water than ordinary tartaric acid, and fuses at 205° (410° F.).

Mesotartaric Acid—*Inactive Tartaric acid*—is obtained by oxidation of erythrol; or by heating dextrotartaric acid with water at 165° (329° F.) for two days.

HIGHER DICARBOXYLIC OXYACIDS.

The carbohydrates, on oxidation with nitric acid, yield *tetroxydicarboxylic acids*: $\text{COOH} \cdot (\text{CHOH})_4 \cdot \text{COOH}$. Among these are: **mannosaccharic acids**, derived from the mannonic acids (p. 343); **saccharic acids**; and **mucic acid**. Of the three saccharic acids the d-acid is the best known. It is produced by oxidation of many carbohydrates, including cane sugar and grape sugar, by nitric acid, and by the action of bromin water on glucuronic acid (p. 348). Nascent H reduces it to glucuronic acid. It forms a syrup or a deliquescent solid, which, on standing, changes to a crystalline lactone. Mucic acid is produced by the oxidation of dulcitol, milk sugar, and the gums. It is a white solid, almost insoluble in cold water and in alcohol, which fuses at 210° (410° F.). When heated it loses CO_2 and forms *pyromucic*, or *furfurane monocarboxylic acid* (p. 510).

Pentoxydicarboxylic acids are also known, of which the type is *pentoxy pimelic acid*: $\text{COOH} \cdot (\text{CHOH})_5 \cdot \text{COOH}$.

OXYTRICARBOXYLIC ACIDS— $\text{C}_n\text{H}_{2n-4}\text{O}_7$.

Citric Acid— $\text{HO} \cdot \text{C} \begin{array}{l} \diagup \text{CH}_2 \cdot \text{COOH} \\ \text{---} \text{COOH} \\ \diagdown \text{CH}_2 \cdot \text{COOH} \end{array}$, exists in the juices of many fruits,

lemon, strawberry, currant, and in small quantity, as calcium citrate, in cow's milk. It is obtained commercially from lemon juice. It crystallizes in large, rhombic prisms, very soluble in water and in alcohol. It fuses at 100° (212° F.); at 175° (347° F.) it is decomposed with loss of water and formation of aconitic acid (p. 431); and at a higher temperature CO_2 is given off and citraconic and itaconic acids are produced. In the body its salts are oxidized to carbonates.

ALDEHYDE-ACIDS.

These are substances having both aldehyde and acid functions, and containing the groups CHO and COOH. The simplest of the class is formic acid, already referred to as the first term of the acetic series (p. 328), in which, however, the carbon atom is common to the two groups: $\text{O} : \text{C} \begin{array}{l} \diagup \text{H} \\ \diagdown \text{OH} \end{array}$.

Glyoxylic Acid— $\text{CHO} \cdot \text{COOH}$ —when produced unites with water to form a hydrate: $(\text{OH})_2 : \text{CH} \cdot \text{COOH}$, corresponding to chloral hydrate (p. 304): $(\text{OH})_2 : \text{CH} \cdot \text{CCl}_3$. This is a thick syrup, or it forms rhombic prisms. It is produced by heating dichloroacetic acid with water at 230° (446° F.): $\text{CHCl}_2 \cdot \text{COOH} + \text{H}_2\text{O} = \text{CHO} \cdot \text{COOH} + 2\text{HCl}$. It has the reducing power and other properties of the aldehydes.

KETONE-ACIDS.

These compounds contain both the ketonic and carboxyl groups, CO and COOH.

The **monoketone-monocarboxylic acids** contain one CO and one COOH. According as the CO group occupies the position adjacent to the carboxyl, or further removed therefrom, these acids are designated as α , β , γ , etc.; thus $\text{CH}_3.\text{CH}_2.\text{CO}.\text{COOH}=\alpha$, $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOH}=\beta$, etc.

The α , γ , δ , etc., acids are much more stable than the β -acids, and may be obtained by oxidation of the corresponding secondary alcohol acids. The α acids are derivable from formic acid by substitution of acidyls for the extra-carboxylic hydrogen: $(\text{CH}_3.\text{CO}).\text{COOH}$.

Pyruvic Acid—*Pyroracemic acid*— $\text{CH}_3.\text{CO}.\text{COOH}$ —is formed by oxidation of α -oxypropionic acid: $2\text{CH}_3.\text{CHOH}.\text{COOH} + \text{O}_2 = 2\text{CH}_3.\text{CO}.\text{COOH} + 2\text{H}_2\text{O}$. It is also formed by distillation of tartaric acid: $\text{COOH}.\text{CHOH}.\text{CHOH}.\text{COOH} = \text{CH}_3.\text{CO}.\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$.

The β -ketone acids are more unstable, and are decomposed by heat with formation of ketone and carbon dioxide: $\text{COOH}.\text{CH}_2.\text{CO}.\text{CH}_3 = \text{CO}_2 + \text{CH}_3.\text{CO}.\text{CH}_3$. Their esters are, however, quite stable, and are employed in many syntheses. The β acids bear the same relation to acetic acid that the α acids do to formic acid: $(\text{CH}_3.\text{CO}).\text{CH}_2.\text{COOH}$.

Aceto-acetic Acid— $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COOH}$ —may be obtained as a thick, strongly acid liquid by saponification of its esters. Heat decomposes it into acetone and carbon dioxide, according to the equation given above. Aceto-acetic acid accompanies β -oxybutyric acid and acetone in the urine in diabetes. (See Aceto-acetic ester, p. 360).

Lævulinic Acid— *β -acetylpropionic acid*— $\text{CH}_3.\text{CO}.\text{CH}_2.\text{CH}_2.\text{COOH}$ —is obtained, along with formic acid, by boiling fructose, or cane-sugar, with dilute H_2SO_4 , and also similarly from pseudomucin: $\text{CH}_2.\text{OH}.\text{CO}.\text{(CHOH)}_3.\text{CH}_2\text{OH} = \text{CH}_3.\text{CO}.\text{CH}_2.\text{CH}_2.\text{COOH} + \text{H}.\text{COOH} + \text{H}_2\text{O}$. It crystallizes in plates, f. p. 33.5° , hygroscopic, very soluble in water, alcohol and ether. By reduction it yields normal valerianic acid.

Diketone-monocarboxylic acids, such as $\text{CH}_3.\text{CO}.\text{CO}.\text{COOH}$, are also known, as well as triketone monocarboxylic acids, and mono-, di-, and triketone dicarboxylic acids. Aldehyde-ketone acids, such as $\text{CHO}.\text{CO}.\text{COOH}$, also exist.

Mesoxalic Acid—*Dioxymalonic acid*— $\begin{array}{c} \text{HO} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{HO} \end{array} \begin{array}{c} \text{COOH} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{COOH} \end{array}$ —is the monoketone-dicarboxylic acid, $\text{COOH}.\text{CO}.\text{COOH}$, combined with water in the same manner as chloral hydrate and glyoxylic acid (see above and pp. 304, 346). Esters are known corresponding to both forms: oxymalonic esters, $\text{CO}:(\text{COO}.\text{C}_2\text{H}_5)_2$; and dioxymalonic esters, $\text{C}(\text{OH})_2:(\text{COO}.\text{C}_2\text{H}_5)_2$. Mesoxalic acid is obtained by the action of

boiling barium hydroxid upon dibromomalonic acid: $\text{COOH.CBr}_2\text{.COOH} + \text{Ba(OH)}_2 = \text{COOH.C(OH)}_2\text{.COOH} + \text{BaBr}_2$, or upon alloxan (mesoxalylurea). It crystallizes in prisms, very soluble in water, fusible at 115° (239° F.) On evaporation of its aqueous solution it decomposes into carbon monoxid, water and oxalic acid; at higher temperatures it yields carbon dioxid and glyoxylic acid.

OXYALDEHYDE AND OXYKETONE ACIDS.

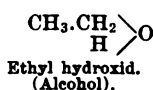
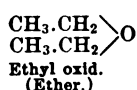
These acids contain alcoholic groups, CH_2OH , CHOH , or COH in addition to carboxyl and either the aldehyde or ketone group, CHO or CO .

Glucuronic Acid— $\text{CHO}(\text{CHOH})_4\text{.COOH}$ —is a derivative of glucose: $\text{CHO}(\text{CHOH})_4\text{.CH}_2\text{OH}$. It is a syrup which passes into a crystalline lactone on warming. It occurs in the urine in small quantity normally, in combination with phenol, skatole and indole, and with camphors, chloral and other substances when these are present.

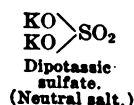
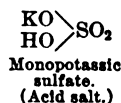
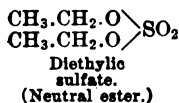
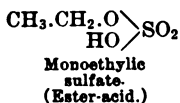
SIMPLE ETHERS.

These substances have been referred to (p. 282) as the simplest products of oxidation of the hydrocarbons. The term *ether* was formerly applied to any substance produced by the action of an acid upon an alcohol. Such products belong, however, to two distinct classes:

(1) The simple ethers, or ethers, which are the oxids of the hydrocarbon radicals, and the counterparts of the metallic oxids, bearing the same relation to the alcohols that the metallic oxids do to their hydroxids:



(2) The compound ethers, now called esters, which are the products of the reaction between an acid and the alcohol, the latter behaving as a basic hydroxid (p. 284). They are the counterparts of the metallic salts:



Mixed ethers differ from simple ethers in that they contain different, in place of similar, alkyls, as methyl-ethyl oxid: $\text{CH}_3\text{.O.CH}_2\text{.CH}_3$.

Simple and mixed ethers are formed: (1) By interaction of the alcohols and alkyl-sulfuric acids. Thus methyl-sulfuric acid and ethylic alcohol form methyl-ethyl oxid: $\text{SO}_2 \begin{smallmatrix} \text{O.CH}_3 \\ \text{OH} \end{smallmatrix} + \text{C}_2\text{H}_5.\text{O.H} = \text{C}_2\text{H}_5.\text{O.CH}_3 + \text{SO}_2:(\text{OH})_2$. (2) By the action of alkyl halids upon sodium alcoholates: $\text{CH}_3.\text{Cl} + \text{C}_2\text{H}_5.\text{O.Na} = \text{NaCl} + \text{C}_2\text{H}_5.\text{O.CH}_3$. (3) By the action of silver oxid upon alkyl halids: $2\text{C}_2\text{H}_5\text{I} + \text{Ag}_2\text{O} = 2\text{AgI} + \text{O}(\text{C}_2\text{H}_5)_2$.

Methyl oxid— $\text{CH}_3.\text{O.CH}_3$ —46—isomeric with ethyl alcohol, is obtained by the action of silver oxid upon methyl iodid, or by the action of H_2SO_4 and boric acid upon methyl alcohol. It is a colorless gas, has an ethereal odor, burns with a pale flame, liquefies at -36° (-32.8° F.), and boils at -21° (-5.8° F.), is soluble in H_2O , H_2SO_4 and ethylic alcohol.

Ethyl Oxid—*Ethylic ether*—*Sulfuric ether*—*Æther fortier* (U.S.); *Æther purus* (Br.)— $\text{C}_2\text{H}_5.\text{O.C}_2\text{H}_5$.—In the manufacture of ether a mixture is made of 5 pts. of 90% alcohol and 9 pts. of concentrated H_2SO_4 , in a vessel surrounded by cold water. This mixture is introduced into a retort, into which a slow stream of alcohol is allowed to flow during the remainder of the process. Heat, so regulated as not to exceed 140° (284° F.), is then applied to the retort, which is connected with a well-cooled condenser, and continued until the temperature rises above the point indicated. The distillate contains ether, alcohol, water and dissolved gases, notably SO_2 . It is shaken with water containing potash or lime, and the ether decanted off. The product is "washed ether." For further purification it is treated with calcium chlorid, or recently burnt lime, with which it is left in contact for 24 hours, and from which it is then distilled.

In the conversion of alcohol into ether, sulfovinic or ethyl-sulfuric acid behaves as a "contact substance" and serves to carry an ethyl radical from one alcohol molecule to another, with formation of water and regeneration of sulfuric acid. In the first stage of the reaction ethyl-sulfuric acid is formed by the action of H_2SO_4 upon alcohol, molecule for molecule: $\text{H}_2\text{SO}_4 + \text{C}_2\text{H}_5.\text{OH} = \text{H}_2\text{O} + \text{C}_2\text{H}_5.\text{HSO}_4$. The ethyl-sulfuric acid then reacts with another molecule of alcohol, according to the general reaction (1) for the formation of ethers, to form ether and sulfuric acid: $\text{C}_2\text{H}_5.\text{HSO}_4 + \text{C}_2\text{H}_5.\text{OH} = \text{H}_2\text{SO}_4 + (\text{C}_2\text{H}_5)_2\text{O}$. It would seem, therefore, that a given quantity of H_2SO_4 could convert an unlimited amount of alcohol into ether. But the gradual accumulation of the H_2O formed in the first stage of the reaction, and the occurrence of secondary reactions in practice limit the amount of ether produced to about four or five times the bulk of acid used.

Ether is a colorless liquid; has a sharp, burning taste, and a peculiar, tenacious odor, characterized as ethereal. Sp. gr. 0.723 at

12.5° (54.5° F.); it boils at 34.5° (94.1° F.). Its tension of vapor is very great, especially at high temperatures; and it is exceedingly volatile. Water dissolves one-ninth its weight of ether. Ethylic and methylic alcohols are miscible with it in all proportions. Ether is an excellent solvent of many substances not soluble in water and alcohol. The resins and fats are readily soluble in ether. The salts of the alkaloids and many vegetable coloring matters are soluble in alcohol and water, but insoluble in ether, while the free alkaloids are for the most part soluble in ether, but insoluble, or very sparingly soluble, in water.

Ether is highly inflammable; and burns with a luminous flame. The vapor forms with air a violently explosive mixture. It is denser than air, through which it falls and diffuses itself to a great distance; caution is therefore required in handling ether in a locality in which there is a light or fire, especially if the fire be near the floor.

Pure ether is neutral in reaction. H_2SO_4 mixes with it, with elevation of temperature, and formation of sulfovinic acid. With sulfuric anhydrid it forms ethyl sulfate. HNO_2 , aided by heat, oxidizes it to carbon dioxid and acetic and oxalic acids. Ether, saturated with HCl and distilled, yields ethyl chlorid. Cl , in the presence of H_2O , oxidizes it, with formation of aldehyde, acetic acid, and chloral. In the absence of H_2O , however, a series of products of substitution are produced, in which 2, 4, and 10 atoms of H are replaced by a corresponding number of atoms of Cl . These substances in turn, by substitution of alcoholic radicals, or of atoms of elements, for atoms of Cl , give rise to other derivatives.

Alkylen Oxids—Ethers of Glycols.—The oxids of the univalent hydrocarbon radicals, the alkyls, correspond to the monohydric alcohols; and similarly the oxids of the bivalent hydrocarbon radicals, which latter are called **alkylens**, correspond to the dihydric alcohols, or glycols. Two classes of these ethers are known: A. **Acyclic alcohol-ethers** of the types: $\text{CH}_2\text{OH}.\text{CH}_2.\text{O}.\text{C}_2\text{H}_5$ =**glycol-ethyl ether**; $\text{C}_2\text{H}_5.\text{O}.\text{CH}_2.\text{CH}_2.\text{O}.\text{C}_2\text{H}_5$ =**glycol-diethyl ether**, and $\text{CH}_2\text{OH}.\text{CH}_2.\text{O}.\text{CH}_2.\text{CH}_2\text{OH}$ =**diethylene-glycol ether**; and B. **Cyclic ethers** of several types, included among the heterocyclic compounds, the simplest of which is: **Ethylene Oxid**— $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{O}$ —which is prepared by

the action of caustic potash on ethylene chlorhydrin (p. 363): $\text{CH}_2\text{OH}.\text{CH}_2\text{Cl} + \text{KHO} = (\text{CH}_2)_2\text{O} + \text{KCl} + \text{H}_2\text{O}$. It is a volatile liquid, boils at 13.5° (54.3° F.), is neutral in reaction and mixes with water. It unites with H_2O to form glycol, and with HCl to regenerate ethylene chlorhydrin. Nascent H converts it into ethyl alcohol.

Two classes of ethers are also derivable from the glycerols:

A. **Acyclic ethers**, such as mono-, di- and triethylins: $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{O}(\text{C}_2\text{H}_5)$; $\text{CH}_2\text{OH} \cdot \text{CHO}(\text{C}_2\text{H}_5) \cdot \text{CH}_2\text{O}(\text{C}_2\text{H}_5)$; and $\text{CH}_2\text{O}(\text{C}_2\text{H}_5) \cdot \text{CHO}(\text{C}_2\text{H}_5) \cdot \text{CH}_2\text{O}(\text{C}_2\text{H}_5)$; and B. **Cyclic ethers**, such as

glycerol ether:
$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \\ | \quad | \quad | \\ \text{O} \quad \text{O} \quad \text{O} \\ | \quad | \quad | \\ \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \end{array}$$
, and **glycid**, or **epichlorhydrin alcohol**:

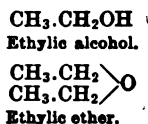
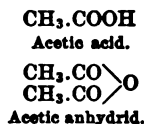
$\text{O} \begin{array}{l} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH}_2\text{OH} \end{array}$, corresponding to epichlorhydrin (p. 364).

ACID ANHYDRIDS.

The acyclic ethers of the glycols and glycerols, referred to above, are properly included in that class of oxidation products of the paraffins derivable from the hydrocarbons by both interpolation of an oxygen atom between two hydrocarbon groups and the oxidation of one or more such groups (p. 282). The esters, which are also included in the same class, will be considered later (p. 358).

Another group of the same class are the **acid anhydrides**. These substances may be considered as being derived from the paraffins by interpolation of an oxygen atom symmetrically, and the oxidation of the two neighboring CH_2 groups to CO groups. Thus acetic anhydrid may be derived from normal butane: $\text{CH}_3 \cdot \text{CO} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$ from $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$.

The acid anhydrids are also the oxids of the acid radicals (acidyls); and bear the same relation to the acids that the simple ethers bear to the alcohols:



The acid anhydrids of the monobasic acids are produced by the action of the acidyl chlorids upon anhydrous salts: $\text{C}_2\text{H}_5\text{O} \cdot \text{OK} + \text{C}_2\text{H}_5\text{O} \cdot \text{Cl} = (\text{C}_2\text{H}_5\text{O})_2\text{O} + \text{KCl}$; or by the action of phosphorus oxychlorid upon the alkali salts of the acids. In this method of formation the acidyl chlorid is first produced: $2\text{C}_2\text{H}_5\text{O} \cdot \text{OK} + \text{POCl}_3 = 2\text{C}_2\text{H}_5\text{O} \cdot \text{Cl} + \text{PO}_3\text{K} + \text{KCl}$; and this acts upon an excess of the salt according to the above equation. Formic acid produces no anhydrid.

Acetic Anhydrid— $(\text{C}_2\text{H}_5\text{O})_2\text{O}$ —is a pungent liquid which boils at 137° (278.6° F.). It is formed by the general methods and also by heating lead acetate with carbon disulfid at 165° (329° F.). It serves for the introduction of the radical acetyl into other molecules.

Mixed anhydrids of the fatty acids, corresponding to the mixed ethers, and containing two different acidyls, are also known, but on heating are split into two anhydrids: $2\text{CH}_3.\text{CH}_2.\text{CO}.\text{O}.\text{CO}.\text{CH}_3 = (\text{CH}_3.\text{CH}_2.\text{CO})_2\text{O} + (\text{CH}_3.\text{CO})_2\text{O}$.

Acid peroxids of the acetic series, containing two interpolated oxygen atoms, such as $\text{CH}_3.\text{CO}.\text{O}.\text{O}.\text{CO}.\text{CH}_3$, exist, but are very unstable.

Anhydrids of oxalic and malonic acids are unknown, but succinic acid readily forms an anhydrid: $\begin{array}{c} \text{CH}_2.\text{CO} \\ | \\ \text{CH}_2.\text{CO} \end{array} \text{O}$. The oxyacids on loss of H_2O tend to form lactids or lactones rather than anhydrids.

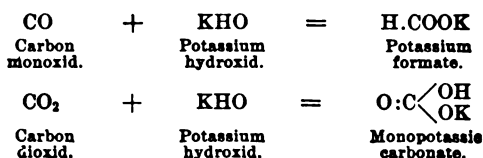
ACIDYL HALIDS.

These compounds, also known as halid anhydrids, are the halogen compounds of the acidyls. They are produced: (1) by the action of the phosphorus halids upon the acids or their salts: $3\text{CH}_3.\text{COOH} + \text{PCl}_3 = 3\text{CH}_3.\text{COCl} + \text{PO}_3\text{H}_3$; or $2\text{CH}_3.\text{COOK} + \text{POCl}_3 = 2\text{CH}_3.\text{COCl} + \text{PO}_3\text{K} + \text{KCl}$; or $\text{CH}_3.\text{COOH} + \text{PCl}_5 = \text{CH}_3.\text{COCl} + \text{POCl}_3 + \text{HCl}$; (2) by the action of phosgene upon the acids, or their salts: $\text{COCl}_2 + \text{CH}_3.\text{COOH} = \text{CH}_3.\text{CO}.\text{Cl} + \text{CO}_2 + \text{HCl}$; (3) by the action of phosphorus pentoxid upon the acids in presence of hydrochloric acid: $3\text{CH}_3.\text{COOH} + 3\text{HCl} + \text{P}_2\text{O}_5 = 3\text{CH}_3.\text{CO}.\text{Cl} + 2\text{PO}_4\text{H}_3$; or, (4) by the action of chlorin upon the aldehydes: $\text{Cl}_2 + \text{CH}_3.\text{CO}.\text{H} = \text{CH}_3.\text{CO}.\text{Cl} + \text{HCl}$.

Acetyl Chlorid— $\text{CH}_3.\text{CO}.\text{Cl}$ —is a colorless, pungent liquid, which boils at 55° (131° F.). It is decomposed by water with formation of acetic and hydrochloric acids. With acetic acid it forms acetic anhydrid. It is used to produce acetyl derivatives.

OXIDS OF CARBON.

The two oxids of carbon are also anhydrids in that they combine with water to produce acids, or, what amounts to the same thing, with KHO to form the K salts, thus:



Carbon Monoxid—Carbonous oxid—Carbonic oxid— CO —28—is formed: (1) By burning C with a limited supply of air. (2) By

passing dry carbon dioxid over red-hot charcoal. (3) By heating oxalic acid with sulfuric acid: $C_2O_4H_2 = H_2O + CO + CO_2$; and passing the gas through sodium hydroxid to separate CO_2 . (4) By heating potassium ferrocyanid with H_2SO_4 .

It is a colorless, tasteless gas: sp. gr. 0.9678A; very sparingly soluble in H_2O and in alcohol. It burns in air with a blue flame to CO_2 , and it forms explosive mixtures with air and oxygen. It is a valuable reducing agent, and is used for the reduction of metallic oxids at a red heat. Ammoniacal solutions of the cuprous salts absorb it readily. Being non-saturated, it unites readily with O to form CO_2 , and with Cl to form $COCl_2$, the latter a colorless, suffocating gas, known as **phosgene**, or **carbonyl chlorid**, which is of service in the formation of acid chlorids and anhydrids (p. 352) and in a variety of other syntheses.

Toxicology.—Carbon monoxid is an exceedingly poisonous gas, and is the chief toxic constituent of the gases given off from blast-furnaces, from defective flues, from open coal or charcoal fires and of illuminating gas.

Poisoning by CO may occur in several ways. By inhalation of the gases discharged from blast-furnaces and from copper-furnaces, the former containing 25 to 32 per cent and the latter 13 to 19 per cent. of CO. By the fumes given off from charcoal burned in a confined space, which consists of a mixture of the two oxids of carbon, the dioxid predominating largely,* especially when the combustion is most active. The following is the composition of an atmosphere produced by burning charcoal in a confined space, and which proved rapidly fatal to a dog: oxygen, 19.19; nitrogen, 76.62; carbon dioxid, 4.61; carbon monoxid, 0.54; marsh-gas, 0.04. Obviously the deleterious effects of charcoal-fumes are more rapidly fatal in proportion as the combustion is imperfect and the room small and ill-ventilated.

A fruitful source of CO poisoning, sometimes fatal, but more frequently producing languor, headache and debility, is to be found in the stoves, furnaces, etc., used in heating our dwellings and other buildings, especially when the fuel is anthracite coal. This fuel produces in its combustion, when the air supply is not abundant, considerable quantities of CO, to which a further addition may be made by the reduction of the dioxid, also formed, in passing over red-hot iron.

Of late years cases of fatal poisoning by illuminating gas are of very frequent occurrence. The most actively poisonous ingredient of illuminating gas is CO, which exists in ordinary coal-gas in the proportion of 4 to 7.5 per cent, and in water-gas, made by decomposing superheated steam by passage over red-hot coke, and subsequent charging with vapor of hydrocarbons, in the large proportion of 30-35 per cent.

The method in which CO produces its fatal effects is by forming with the blood-coloring matter a compound which is more stable than oxyhæmoglobin, and thus causing asphyxia by destroying the power of the blood corpuscles of carrying O from the air to the tissues. This compound of CO and hæmoglobin is quite stable, and hence the symptoms of this form of poisoning are very persistent, lasting until the place of the coloring-matter thus rendered useless is supplied by new formation. The prognosis is very unfavorable when the amount of the gas inhaled has been at all considerable, the treatment usually followed, *i. e.*, artificial respiration and inhalation of O, restoring the altered coloring matter very slowly. There would seem to be no form of poisoning in which transfusion of blood is more directly indicated than in that by CO, but it has been found to be detrimental rather than beneficial.

Detection after death.—The blood of those asphyxiated by CO is persistently bright-red in color. When suitably diluted and examined with the spectroscope, it presents an absorption spectrum (No. 6, fig. 43, p. 661) of two bands similar to that of oxyhæmoglobin (No. 3, fig. 43), but in which the two bands are more equal and somewhat nearer the violet end of the spectrum. Owing to the greater stability of the CO compound, its spectrum may be readily distinguished from that of the O compound by the addition of a reducing agent (an ammoniacal solution of ferrous tartrate), which changes the spectrum of oxyhæmoglobin to the single-band spectrum of hæmoglobin (No. 1, fig. 43), while that of the CO compound remains unaltered, or only fades partially.

If a solution of caustic soda of sp. gr. 1.3 be added to normal blood, a black, slimy mass is formed, which, when spread upon a white plate, has a greenish-brown color. The same reagent added to blood altered by CO forms a firmly clotted mass, which in thin layers upon a white surface is bright red in color.

A piece of gun-cotton upon which platinum-black has been dusted fires in air containing 2.5 in 1,000 of CO.

Carbon Dioxid—Carbonic anhydrid—Carbonic acid gas—CO₂—44—is obtained: (1) By burning C in air or O. (2) By decomposing a carbonate (marble=CaCO₃) by a mineral acid (HCl diluted with an equal volume of H₂O).

At ordinary temperatures and pressures it is a colorless, suffocating gas; has an acidulous taste; sp. gr. 1.529 A; soluble in an equal volume of H₂O at the ordinary pressure, much more soluble as the pressure increases. **Soda water** is a solution of carbonic acid in H₂O under increased pressure. When compressed to the extent of 38 atmospheres at 0° (32° F.); 50 atm. at 15° (59° F.); or 73 atm. at 30° (86° F.) it forms a transparent, mobile liquid, by whose evapo-

ration, when the pressure is relieved, sufficient cold is produced to solidify a portion into a snow-like mass, which, by spontaneous evaporation in air, produces a temperature of -90° (-130° F.).

Carbon dioxid neither burns nor does it support combustion. When heated to $1,300^{\circ}$ ($2,370^{\circ}$ F.), it is dissociated into CO and O. A similar decomposition is brought about by the passage through it of electric sparks. When heated with H it yields CO and H_2O . When K, Na, or Mg is heated in an atmosphere of CO_2 , the gas is decomposed with formation of a carbonate and separation of carbon. When caused to pass through solutions of the hydroxids of Na, K, Ca, or Ba, it is absorbed, with formation of the carbonates of those metals, which, in the case of the last two, are deposited as white precipitates. Solution of potash is frequently used in analysis to absorb CO_2 , and lime and baryta water as tests for its presence. The hydroxids mentioned also absorb CO_2 from moist air.

Atmospheric Carbon Dioxid.—Carbon dioxid exists in free country air in the proportion of about four parts in 10,000. Its sources are from: (1) Respiration. Expired air contains about 4.5 per cent CO_2 . (2) Combustion of fuel, illuminating gas, etc. A burner consuming three cubic feet of illuminating gas per hour produces as much CO_2 as is formed by the respiration of seven human beings. In a confined space respiration and combustion vitiate the air in two ways: by addition of carbon dioxid and by removal of oxygen, as the CO_2 is produced at the expense of atmospheric oxygen. By the other methods of its origin it is merely added to the air, whose oxygen-content remains nearly unaltered. (3) Fermentation. For every liter of alcohol produced 384 liters of CO_2 are added to the air. (4) Tellural sources, such as volcanic fissures, volcanoes, spring waters. (5) Manufacturing operations, such as lime-burning, cement and brick-making, iron furnaces, etc. (6) In coal mines the *after-damp* contains a volume of CO_2 equal to that of the fire-damp exploded.

Notwithstanding the large amounts of CO_2 discharged into the atmosphere from these several sources, and it is estimated that the amount is sufficient to double the atmospheric CO_2 -content in about eighty years, no increase in the normal proportion of CO_2 in free air has been observed. This is due to the constant removal of CO_2 from the air by plants, the green pigment of which, chlorophyll, decomposes CO_2 under the influence of sunlight, retaining the carbon in organic combination, and returning oxygen to the air.

Action on the Economy.—An animal introduced into an atmosphere of pure CO_2 dies almost instantly, and without entrance of the gas into the lungs, death resulting from spasm of the glottis, and consequent apnœa.

When the proportion of O is not diminished, the poisonous action

of CO_2 is not as manifest, in equal quantities, as when the air is poorer in oxygen. An animal will die rapidly in an atmosphere composed of 21 per cent. O, 59 per cent. N, and 20 per cent. CO_2 by volume; but will live for several hours in an atmosphere whose composition is 40 per cent. O, 37 per cent. N, 23 per cent. CO_2 . If CO_2 be added to normal air, of course the relative quantity of O is slightly diminished, while its absolute quantity remains the same. This is the condition of affairs existing in nature when the gas is discharged into the air. Under these circumstances an addition of 10–15 per cent. of CO_2 renders an air rapidly poisonous, and one of 5–8 per cent. will cause the death of small animals more slowly. Even a less proportion than this may become fatal to an individual not habituated.

When present in large proportion, CO_2 produces immediate loss of muscular power, and death without a struggle; when more dilute, a sense of irritation of the larynx, drowsiness, pain in the head, giddiness, gradual loss of muscular power, and death in coma.

If the CO_2 present in air be produced by respiration, or combustion, the proportion of O is at the same time diminished, and much smaller absolute and relative amounts of the poisonous gas will produce the effects mentioned above. Thus, an atmosphere containing in volumes 19.75 per cent. O, 74.25 per cent. N, 6 per cent. CO_2 , is much more rapidly fatal than one composed of 21 per cent. O, 59 per cent. N, 20 per cent. CO_2 . With a corresponding reduction of O, 5 per cent. of CO_2 renders an air sufficiently poisonous to destroy life; 2 per cent. produces severe suffering; 1 per cent. causes great discomfort, while 0.1 per cent., or even less, is recognized by a sense of closeness.

The treatment in all cases of poisoning by CO_2 consists in the inhalation of pure air (to which an excess of O may be added), aided, if necessary, by artificial respiration, the cold douche, galvanism, and friction.

Detection of Carbon Dioxid and Analysis of Confined Air.—Carbon dioxid, or air containing it, causes a white precipitate when caused to bubble through lime or baryta water. Normal air contains enough of the gas to form a scum upon the surface of these solutions when exposed to it.

It was at one time supposed that air in which a candle continued to burn was also capable of maintaining respiration. This is, however, by no means necessarily true. A candle introduced into an atmosphere in which the normal proportion of O is contained, burns readily in the presence of 8 per cent. of CO_2 ; is perceptibly dulled by 10 per cent.; is usually extinguished with 13 per cent.; always extinguished with 16 per cent. Its extinction is caused by a less proportion of CO_2 , 4 per cent., if the quantity of O be at the same time

diminished. Moreover, a contaminated atmosphere may not contain enough CO_2 to extinguish, or perceptibly dim the flame of a candle, and at the same time contain enough of the monoxid to render it fatally poisonous if inhaled.

The presence of CO_2 in a gaseous mixture is determined by its absorption by a solution of potash; its quantity either by measuring the diminution in bulk of the gas, or by noting the increase in weight of an alkaline solution.

To determine the proportions of the various gases present in air the apparatus shown in Fig. 42 is used. A is an aspirator of known capacity, filled with water at the beginning of the operation. It connects by a flexible tube from its upper part with an absorbing apparatus consisting of *a*, a U-shaped tube containing fragments of pumice-stone, moistened with H_2SO_4 ; by the increase in weight of this tube the weight of watery vapor in the volume of air drawn through by the aspirator is determined; *b*, a Liebig's bulb filled with a solution of potash; *c*, a U-tube filled with fragments of pumice moistened with H_2SO_4 ; *b* and *c* are weighed together and their increase in weight is the weight of CO_2 in the volume of air operated

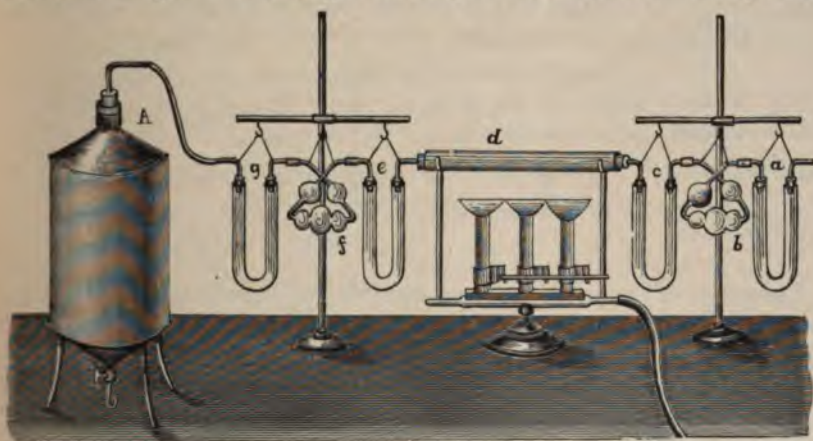


FIG. 42.

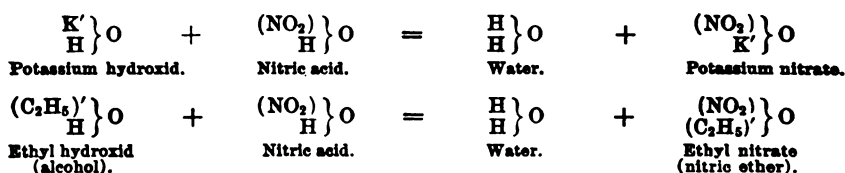
on. Every gram of increase in weight represents 0.50607 litre, or 31.60356 cubic inches; *d* is a tube of difficultly fusible glass, filled with black oxid of copper and heated to redness; *e* is a U-tube filled with pumice moistened with H_2SO_4 ; its increase in weight represents H_2O obtained from decomposition of CH_4 . Every gram of increase in weight of *e* represents 0.444 gram, or 0.621 litre, or 38.781 cubic inches of marsh-gas; *f* and *g* are similar to *b* and *c*, and their increase in weight represents CO_2 formed by oxidation of CO and CH_4 in *d*.

From this the amount of CO is thus calculated: First, 2.75 grams are deducted from the increase of weight of *f* and *g* for each gram of CH₄ found by *e*; of the remainder, every gram represents 0.6364 gram, or 0.5085 litre, or 31.755 cubic inches of CO. The air is drawn through the apparatus by opening the stopcock of A to such an extent that about thirty bubbles a minute pass through *b*.

As the proportion of CO₂ in air is determinable readily and accurately, its determination in a confined air is depended upon to judge of the respirability of the air and the degree of perfection of the methods of ventilation used. For these purposes an air is condemned as vitiated if it contain more than six parts in 10,000 of CO₂.

ESTERS—COMPOUND ETHERS.

As the alcohols resemble the mineral bases, and the organic acids resemble those of mineral origin, so the esters are similar in constitution to the salts, being *formed by the double decomposition of an alcohol with an acid, mineral or organic*, as a salt is formed by double decomposition of an acid and a mineral base, the radical playing the part of an atom of corresponding valence :



Therefore *the esters are substances derived from acids by partial or complete substitution of an alkyl or alkyls for the basic hydrogen of the acid.*

Some of the esters still contain a portion of the acid hydrogen which, being replaceable by another radical or by a metal, communicates acid qualities to the substance, which is at the same time an ester and a true acid. Such esters are the counter-parts of the acid salts. Or di- and polyhydric alcohols, in combining with acids of inferior basicity, may form esters which still retain alcoholic hydroxyls, and which are, therefore, **alcohol-esters**.

ESTERS OF THE MONOHYDRIC ALCOHOLS.

These esters are produced:

(1) By the action of the acid upon the alcohol: $\text{H}_2\text{SO}_4 + \text{CH}_3.\text{CH}_2-$

$\text{OH}=\text{CH}_3.\text{CH}_2.\text{HSO}_4+\text{H}_2\text{O}$; or $\text{H}_2\text{SO}_4+2\text{CH}_3.\text{CH}_2\text{OH}=(\text{CH}_3.\text{CH}_2)_2\text{SO}_4+2\text{H}_2\text{O}$.

(2) By the action of the corresponding haloid esters upon the silver salt of the acid: $\text{AgNO}_3+\text{C}_2\text{H}_5\text{I}=\text{AgI}+\text{C}_2\text{H}_5.\text{NO}_3$.

(3) By the action of the acidyl chlorids upon the sodium derivatives of the alcohols, and in some instances upon the alcohols themselves: $\text{C}_2\text{H}_5\text{O}.\text{Cl}+\text{C}_2\text{H}_5.\text{O}.\text{Na}=\text{NaCl}+\text{C}_2\text{H}_5\text{O}_2.\text{C}_2\text{H}_5$.

All esters are decomposed into acid and alcohol by the action of water at high temperatures, or of caustic potash or soda: $(\text{C}_2\text{H}_5)\text{NO}_3+\text{KHO}=\text{KNO}_3+\text{C}_2\text{H}_5\text{HO}$.

As this decomposition is analogous to that utilized in the manufacture of soap (p. 366), it is known as **saponification**, and whenever an ester is so decomposed it is said to be **saponified**. When the decomposition is effected by H_2O the free acid and the alcohol are formed, and it is known as **hydrolysis** (p. 116): $(\text{C}_2\text{H}_5)\text{C}_2\text{H}_5\text{O}_2+\text{H}_2\text{O}=\text{C}_2\text{H}_5.\text{HO}+\text{H}.\text{C}_2\text{H}_5\text{O}_2$. This reaction is reversible and therefore does not proceed to completion. Starting with the ester it is saponified according to the equation until equilibrium is established, but starting with alcohol and acid the reaction proceeds according to the equation read from right to left until the same condition is reached.

Ethyl Nitrate—*Nitric ether*— $\text{C}_2\text{H}_5\text{O}-\overset{\text{NO}_2}{\text{O}}$ —91.—A colorless liquid; has a sweet taste and bitter after-taste; sp. gr. 1.112 at 17° (62.6° F.); boils at 85° (185° F.); gives off explosive vapors. Prepared by distilling a mixture of HNO_3 and $\text{C}_2\text{H}_5\text{O}$ in the presence of urea.

Ethyl Nitrite—*Nitrous ether*— $\text{C}_2\text{H}_5\text{O}-\overset{\text{NO}}{\text{O}}$ —75—is prepared by directing nitrous fumes into alcohol, contained in a retort connected with a well-cooled receiver.

It is a yellowish liquid; has an apple-like odor, and a sharp, sweetish taste: sp. gr. 0.947; boils at 18° (64.4° F.); gives off inflammable vapor; very sparingly soluble in H_2O ; readily soluble in alcohol and ether. It is decomposed by warm H_2O and by alkalis.

Ethyl Sulfates— $(\text{C}_2\text{H}_5)\text{HSO}_4$ —*Ethyl sulfuric* or *sulfovinic acid* and $(\text{C}_2\text{H}_5)_2\text{SO}_4$ —*Ethyl sulfate*—*Sulfuric ether*.

Monoethylic sulfate—*Ethyl - sulfuric acid*— $\text{C}_2\text{H}_5.\text{O}\rangle\text{SO}_2$ —is formed as an intermediate product in the manufacture of ethylic ether. It is a colorless, syrupy, highly acid liquid; sp. gr. 1.316; soluble in water and alcohol in all proportions, insoluble in ether.

It decomposes slowly at ordinary temperatures, more rapidly when heated. When heated with alcohol, it yields ethylic ether and H_2SO_4 . When heated with H_2O , it yields alcohol and H_2SO_4 . It forms crystalline salts, known as **sulfovinates**, or **sulfethylates**, one of which, **sodium sulfovinate** $(\text{C}_2\text{H}_5)\text{NaSO}_4$, has been used in medicine. It is a white, deliquescent solid; soluble in H_2O .

Ethyl Sulfate— $(C_2H_5)_2SO_4$ —the true sulfuric ether, is obtained by passing vapor of SO_3 into *pure* ethylic ether, thoroughly cooled. It is a colorless, oily liquid; has a sharp, burning taste, and the odor of peppermint; sp. gr. 1.120. It cannot be distilled without decomposition. With H_2O it forms sulfovinic acid.

Sulfurous and Hyposulfurous Esters.—These compounds have recently assumed medical interest from their relationship to mercaptan, sulfonal and a number of aromatic derivatives used as medicines.

There exist two isomeric sulfurous acids (p. 144), both of which yield neutral esters, but only one of which, the unsymmetrical, $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} S \begin{smallmatrix} H \\ OH \end{smallmatrix}$, forms acid esters. These acid esters are known as **sulfonic acids**. (See Aromatic sulfonic acids, mercaptan, sulfones, sulfonal.)

Diethyl Sulfite— $(C_2H_5)_2SO_3$ —is produced by the action of thionyl chlorid on absolute alcohol: $SOCl_2 + 2C_2H_5HO = SO_3(C_2H_5)_2 + 2HCl$. It is a colorless liquid, having a powerful odor: sp. gr. 1.085, boils at 161° ($321.8^\circ F.$). H_2O decomposes it into alcohol and sulfurous acid.

Ethyl Sulfonic Acid— $SO_2 \begin{smallmatrix} C_2H_5 \\ OH \end{smallmatrix}$ —is formed by the action of ethyl iodid on potassium sulfite: $C_2H_5I + SO_3K_2 = C_2H_5.SO_2OK + KI$. It forms salts and esters.

Sulfinic Acids—are the acid esters of hyposulfurous acid $SO \begin{smallmatrix} H \\ OH \end{smallmatrix}$, and are analogous to the sulfonic acids.

Ethyl Acetate—**Acetic ether**—**Æther aceticus**—(U. S.)— $\begin{smallmatrix} C_2H_5O \\ C_2H_5 \end{smallmatrix} O$ —is obtained by distilling a mixture of sodium acetate, alcohol and H_2SO_4 ; or by passing carbon dioxid through an alcoholic solution of potassium acetate.

It is a colorless liquid, has an agreeable, ethereal odor: boils at 74° ($165.2^\circ F.$); sp. gr. 0.92 at 15° ($59^\circ F.$); soluble in 6 pts. water, and in all proportions in methyl and ethyl alcohols and in ether; a good solvent of essences, resins, cantharidin, morphin, gun cotton, and in general, of substances soluble in ether; burns with a yellowish-white flame. Chlorin acts energetically upon it, producing products of substitution, varying according to the intensity of the light from $C_4H_6Cl_2O_2$ to $C_4Cl_8O_2$.

Ethyl Aceto-acetate—**Aceto-acetic ester**— $CH_3.CO.CH_2.COO-(C_2H_5)$ —is the most important representative of the class of β -ketonic acid esters (p. 347), which are important synthetic reagents. It is prepared by dissolving 6 pts. of metallic sodium in 200 pts. of anhydrous ethyl acetate, distilling off the excess of the ester, mixing the residue with 50 per cent acetic acid in slight excess, decanting the oil which separates, and fractioning.

The formation of aceto-acetic ester in this process occurs in several reactions, the sum of which may be expressed by the equation: $2\text{CH}_3.\text{COO}(\text{C}_2\text{H}_5) = \text{CH}_3.\text{CO}.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5) + \text{CH}_3.\text{CH}_2\text{OH}$; two molecules of ethyl acetate forming one molecule of aceto-acetic ester and one of ethylic alcohol. In one stage of the reaction sodium acts upon ethyl acetate to form ethyl acetyl-sodacetate, sodium ethylate and hydrogen: $2\text{CH}_3.\text{COO}(\text{C}_2\text{H}_5) + \text{Na}_2 = \text{CH}_3.\text{CO}.\text{CHNa}.\text{COO}(\text{C}_2\text{H}_5) + \text{C}_2\text{H}_5.\text{O}.\text{Na} + \text{H}_2$. In another, sodium ethylate acts upon ethyl acetate to form ethyl acetyl-sodacetate and ethylic alcohol: $2\text{CH}_3.\text{COO}(\text{C}_2\text{H}_5) + \text{C}_2\text{H}_5.\text{O}.\text{Na} = \text{CH}_3.\text{CO}.\text{CHNa}.\text{COO}(\text{C}_2\text{H}_5) + 2\text{CH}_3.\text{CH}_2\text{OH}$; and, when the operation is properly conducted, little or no hydrogen is evolved, because that produced in the above reaction acts with sodium upon ethyl acetate to form sodium ethylate: $\text{CH}_3.\text{COO}(\text{C}_2\text{H}_5) + \text{Na}_2 + \text{H}_2 = 2\text{C}_2\text{H}_5.\text{O}.\text{Na}$. The aceto-acetic ester is liberated from its sodium derivative by acetic acid: $\text{CH}_3.\text{CO}.\text{CHNa}.\text{COO}(\text{C}_2\text{H}_5) + \text{CH}_3.\text{COOH} = \text{CH}_3.\text{COONa} + \text{CH}_3.\text{CO}.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$.

Aceto-acetic ester is a colorless liquid, having a pleasant odor, b. p. 181° , almost insoluble in water, and much more stable than the free acid. It is colored violet by Fe_2Cl_6 .

Malonic Ester—Neutral ethyl malonate— $\text{COO}(\text{C}_2\text{H}_5).\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$ —is obtained by the action of HCl upon potassium cyanoacetate, or malonic acid, and alcohol: $\text{CH}_2\text{CN}.\text{COOK} + 2\text{CH}_3.\text{CH}_2\text{OH} + \text{HCl} = \text{KCl} + \text{NH}_3 + \text{COO}(\text{C}_2\text{H}_5).\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$, or $\text{COOH}.\text{CH}_2.\text{COOH} + 2\text{CH}_3.\text{CH}_2\text{OH} = \text{COO}(\text{C}_2\text{H}_5).\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5) + 2\text{H}_2\text{O}$. It is a colorless liquid, b. p. 198° , sp. gr. 1.07, insoluble in water and in alkaline solutions.

When, as in the cases of aceto-acetic and malonic esters, an ester is referred to without designation of the contained alkyl, the neutral ethyl ester is always understood.

The esters of the ketonic acids and neutral malonic ester have this in common, that they contain a CH_2 group between two CO groups, and because of such position this CH_2 group is more labile than the same group otherwise placed, as in hydrocarbons, acids, aldehydes, etc. Its hydrogen is removable to produce products of substitution and of condensation. By the successive action of sodium and alkyl halids upon these esters, many products of substitution are obtained. First an atom of Na replaces a H atom: $\text{CH}_3.\text{CO}.\text{CHNa}.\text{COO}(\text{C}_2\text{H}_5)$ and $\text{COO}(\text{C}_2\text{H}_5).\text{CHNa}.\text{COO}(\text{C}_2\text{H}_5)$. The second H atom in CHNa cannot be directly replaced by Na . But by the action of an alkyl halid the alkyl replaces the Na atom: $\text{CH}_3.\text{CO}.\text{CH}(\text{CH}_3).\text{COO}(\text{C}_2\text{H}_5)$ and $\text{COO}(\text{C}_2\text{H}_5).\text{CH}(\text{CH}_3).\text{COO}(\text{C}_2\text{H}_5)$, and in the compounds so formed the second hydrogen atom is replaceable by Na : $\text{CH}_3.\text{CO}.\text{CNa}(\text{CH}_3).\text{COO}(\text{C}_2\text{H}_5)$ and $\text{COO}(\text{C}_2\text{H}_5).\text{CNa}(\text{CH}_3).\text{COO}(\text{C}_2\text{H}_5)$ and, finally, in these the Na is replaceable by alkyls: $\text{CH}_3.\text{CO}.\text{C}(\text{CH}_3)_2.$

$\text{COO}(\text{C}_2\text{H}_5)$ and $\text{COO}(\text{C}_2\text{H}_5).\text{C}(\text{CH}_3)_2.\text{COO}(\text{C}_2\text{H}_5)$. The compounds so obtained are the mono- and dialkyl aceto-acetic and malonic esters.

The mono- and dialkyl aceto-acetic esters and the original β ketonic esters, are not simply saponified by heating with dilute alkalis, as is usual with esters, but are decomposed in two ways: In the ketonic decomposition they split at the COO group to form ketones: $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5) + 2\text{KHO} = \text{CH}_3.\text{CO}.\text{CH}_3 + \text{CO}_2\text{K}_2 + \text{CH}_3.\text{CH}_2.\text{OH}$; and in the acid decomposition they split at the CO group to form an acetate and a salt of a mono- or dialkyl acetic acid (p. 330): $\text{CH}_3.\text{CO}.\text{C}(\text{CH}_3)_2.\text{COO}(\text{C}_2\text{H}_5) + 2\text{KHO} = \text{CH}_3.\text{COOK} + (\text{CH}_3)_2.\text{CH}.\text{COOK} + \text{CH}_3.\text{CH}_2.\text{OH}$.

The mono- and dialkyl malonic esters, which are the esters of the superior homologues of malonic acid of the isosuccinic type (p. 337), are similarly obtained by the successive action of sodium and alkyl halids upon malonic ester. When hydrolysed or heated they do not undergo the ketonic decomposition, but only the acid decomposition, splitting off CO_2 and forming mono- or dialkyl acetic acids: $\text{COO}(\text{C}_2\text{H}_5).\text{C}(\text{CH}_3)_2.\text{COO}(\text{C}_2\text{H}_5) + 2\text{H}_2\text{O} = (\text{CH}_3)_2.\text{CH}.\text{COOH} + \text{CO}_2 + 2\text{CH}_3.\text{CH}_2.\text{OH}$. The above reactions are utilized to obtain both mono- and dicarboxylic acids.

The esters of the β ketonic acids are converted by nascent hydrogen into β oxyacids. Thus aceto-acetic ester yields β oxybutyric ester: $\text{CH}_3.\text{CO}.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5) + \text{H}_2 = \text{CH}_3.\text{CHOH}.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$.

Of the many condensation reactions of these esters we may mention two: We have seen (p. 301) that formic aldehyde, $\text{H}.\text{CHO}$, readily parts with its O to form condensed products. With aceto-acetic ester it forms methylene aceto-acetic ester: $\text{H}_2\text{C}:\text{C} \begin{smallmatrix} \text{COO}(\text{C}_2\text{H}_5) \\ \text{CO}.\text{CH}_3 \end{smallmatrix}$, or methylene diaceto-acetic ester: $\begin{smallmatrix} (\text{C}_2\text{H}_5)\text{OOC} \\ \text{H}_3\text{C}.\text{OC} \end{smallmatrix} \text{CH}.\text{CH}_2.\text{CH} \begin{smallmatrix} \text{COO}(\text{C}_2\text{H}_5) \\ \text{CO}.\text{CH}_3 \end{smallmatrix}$. Similarly with malonic ester it forms methylene dimalonic ester: $\begin{smallmatrix} (\text{C}_2\text{H}_5)\text{OOC} \\ (\text{C}_2\text{H}_5)\text{OOC} \end{smallmatrix} \text{CH}.\text{CH}_2.\text{CH} \begin{smallmatrix} \text{COO}(\text{C}_2\text{H}_5) \\ \text{COO}(\text{C}_2\text{H}_5) \end{smallmatrix}$. Aceto-acetic ester condenses with urea to form methyluracil, and malonic acid to form malonyl-urea each of which constitutes an important stage in a synthesis of uric acid (p. 529).

The inferior homologue of aceto-acetic acid, **formyl acetic acid**, has not the ketonic structure, $\text{H}.\text{CO}.\text{CH}_2.\text{COOH}$, but the unsaturated constitution, $\text{HO}.\text{CH}:\text{CH}.\text{COOH}$. Its Na compound, $\text{NaH}.\text{CH}:\text{CH}.\text{COONa}$, is formed by dropping a mixture of formic and acetic esters upon Na under ether. This and the corresponding ethyl ester are used in several condensation syntheses of cyclic compounds.

Amyl Nitrate— $\begin{smallmatrix} \text{NO}_2 \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \text{O}$ —obtained by distilling a mixture of

HNO_3 and amyl alcohol in the presence of a small quantity of urea. It is a colorless, oily liquid; sp. gr. 0.994 at 10° (50°F.); boils at 148° (298.4°F.) with partial decomposition.

Amyl Nitrite—Amyl nitris (U. S.)— $\text{C}_5\text{H}_{11}\{\text{NO}\}\text{O}$ —117—prepared by directing nitrous fumes into amyl alcohol, contained in a retort heated over a water-bath; purifying the distillate by washing with an alkaline solution, and rectifying.

It is a slightly yellowish liquid; sp. gr. 0.877; boils at 95° (203°F.). Its vapor, which is orange-colored, explodes when heated to 260° (500°F.). It is insoluble in water; soluble in alcohol in all proportions. Alcoholic solution of potash decomposes it slowly, with formation of potassium nitrite and ethyl and amyl oxids. When dropped upon fused potash, it ignites and yields potassium valerianate.

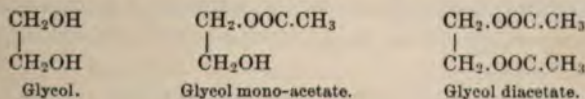
Amyl Acetate—Pear oil— $\text{C}_5\text{H}_{11}\{\text{C}_2\text{H}_3\text{O}\}\text{O}$ —is prepared by distilling a mixture of sulfuric acid, amyl alcohol and potassium acetate. It has the odor of pears, is insoluble in water, soluble in alcohol; and boils at 125° (257°F.). It is used as a flavoring agent and as a solvent for celluloid.

Cetyl Palmitate—Cetin— $\text{C}_{16}\text{H}_{33}\{\text{C}_{16}\text{H}_{31}\text{O}\}\text{O}$ —480—is the chief constituent of **spermaceti**=cetaceum (U. S., Br.), which, besides cetin, contains esters of palmitic, stearic, myristic, and laurostearic acids; and of the alcohols: **lethol**, $\text{C}_{12}\text{H}_{25}\text{O}$; **methol**, $\text{C}_{14}\text{H}_{29}\text{O}$; **ethol**, $\text{C}_{15}\text{H}_{31}\text{O}$, and **stethol**, $\text{C}_{18}\text{H}_{37}\text{O}$.

Melissyl Palmitate—*Melissin*— $\text{C}_{16}\text{H}_{31}\{\text{C}_{30}\text{H}_{61}\}\text{O}$ —676.—Beeswax consists mainly of two substances: **cerotic acid**, $\text{C}_{27}\text{H}_{53}\text{O.OH}$, soluble in boiling alcohol, and **melissyl palmitate**, insoluble in that liquid. **China wax** consists chiefly of **ceryl cerotate**, $\text{C}_{27}\text{H}_{53}\text{O}_2$ ($\text{C}_{27}\text{H}_{55}$).

ESTERS OF DIHYDRIC ALCOHOLS OR GLYCOLS.

The glycols behave as diacid bases and form with the monobasic acids basic and also neutral esters:



The **haloid esters** of the glycols are also basic or neutral. The basic compounds are the **glycol halohydrins**, e. g., $\text{CH}_2\text{OH}.\text{CH}_2\text{Cl}$ =**Ethylene chlorhydrin**, produced by the action of the hydric acids upon the glycols, or upon ethylene oxid and its homologues.

The neutral haloid esters are among the haloid derivatives of the

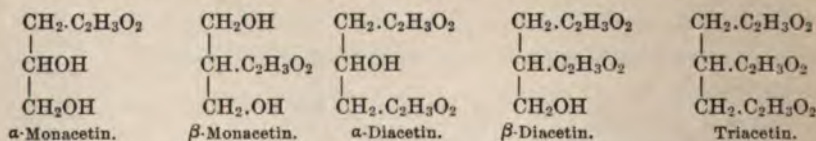
paraffins, higher than the first (pp. 277-281). They are produced by (1) the substitution of the halogen in the paraffin or in the monohalogen paraffin; thus ethyl chlorid: $\text{CH}_3.\text{CH}_2\text{Cl}$ yields ethylene chlorid; $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$; (2) by addition of the halogens to the olefins (p. 424), thus ethylene: $\text{CH}_2:\text{CH}_2$ yields ethylene bichlorid; $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$; (3) by the action of the hydracids upon the monohalogen olefins, or upon the glycols, or upon the glycol chlorhydrins. Thus ethylene bichlorid is obtained from ethylene monochlorid: $\text{CHCl}:\text{CH}_2$; ethylene glycol: $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$; or ethylene chlorhydrin: $\text{CH}_2\text{OH}.\text{CH}_2\text{Cl}$. By this latter method two isomeres: $\text{CHCl}_2.\text{CH}_3$ and $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ may be produced.

The neutral haloid esters of the glycols are the starting points in the preparation of the glycols: $\text{CH}_2\text{Br}.\text{CH}_2\text{Br} + 2\text{AgHO} = 2\text{AgBr} + \text{CH}_2\text{OH}.\text{CH}_2\text{OH}$. Nascent hydrogen converts them into the paraffins: $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl} + 2\text{H}_2 = 2\text{HCl} + \text{CH}_3.\text{CH}_3$.

Ethylene Chlorid—Elayl chlorid—Dutch liquid— $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ —is obtained by passing ethylene through a retort in which chlorin is generated. It is a colorless, oily liquid, has a sweetish taste and an ethereal odor; boils at 84° (183.2°F.). It is capable of fixing other atoms of chlorin by substitution to form a series of compounds, the most highly chlorinated of which is **carbon trichlorid**, C_2Cl_6 .

ESTERS OF THE TRIHYDRIC ALCOHOLS OR GLYCEROLS—GLYCERIDS.

The glycerols behave as triacid bases, forming three series of esters with the monobasic acids. These esters are the **mono-**, **di-**, and **triglycerids**. Moreover, as two of the hydroxyls of the alcohol are in the primary groups CH_2OH , while the third is in the secondary group, CHOH , there are two isomeres of each mono- and diglycerid:



The haloid esters are known as the **glycerol halohydrins**. Of the glycerol esters of mineral oxyacids those of nitric and phosphoric acids are of interest.

Glycerol trinitrate—Nitroglycerine—Glonoin— $\text{C}_3\text{H}_5(\text{NO}_3)_3$ —is formed by the action of a mixture of H_2SO_4 and HNO_3 upon glycerol. It is an odorless, yellowish oil; has a sweetish taste; sp. gr. 1.6; insoluble in water, soluble in alcohol and in ether; not volatile; crystallizes in prismatic needles when kept for some time at 0° (32°F.); fuses again at 8° (46.4°F.). When suddenly heated, or when sub-

jected to shock it is explosively decomposed into CO_2 ; N_2 ; H_2O and O . Alkalies saponify it to glycerol and a nitrate.

Nitroglycerol is mixed with diatomaceous earth and with other inert, absorbent substances in dynamite and in other high explosives; and, combined with nitrocellulose, it forms "smokeless powder."

It is used in medicine as a cardiac stimulant, and, in overdose, is an active poison, producing effects somewhat similar to those caused by strychnin.

Glycero-phosphoric Acid— $\text{C}_3\text{H}_5(\text{OH})_2.\text{O}.\text{PO}_3\text{H}_2$ —is the mono-glycerid of phosphoric acid. It is a product of decomposition of the lecithins, or phosphorized fats (p. 367), or may be formed by mixing glycerol and metaphosphoric acid. It is a thick syrup, which is decomposed into glycerol and phosphoric acid when heated with water. It is a dibasic acid.

Glycerol Esters of Organic Acids.—The triacid glycerol esters of the acids of the acetic and acrylic series containing an even number of carbon atoms occur in the animal and vegetable fats and oils.

Tributyrin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_4\text{H}_7\text{O})_3$ —302—exists in butter. It may also be obtained by heating glycerol with butyric acid and H_2SO_4 . It is a pungent liquid, very prone to decomposition, with liberation of butyric acid.

Tricaproin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_6\text{H}_{11}\text{O})_3$ —386—**Tricaprylin**— $\text{C}_3\text{H}_5(\text{O}.\text{C}_8\text{H}_{15}\text{O})_3$ —470—and **Tricaprin**— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{10}\text{H}_{19}\text{O})_3$ —554—exist in small quantities in milk, butter, and cocoa butter.

Tripalmitin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{16}\text{H}_{31}\text{O})_3$ —806—exists in most animal and vegetable fats, notably in palm oil. It may also be obtained by heating glycerol with 8 to 10 times its weight of palmitic acid for 8 hours at 250° ($482^\circ\text{F}.$). It forms crystalline plates, very sparingly soluble in alcohol, even when boiling; very soluble in ether. It fuses at 50° ($122^\circ\text{F}.$), and solidifies again at 46° ($114.8^\circ\text{F}.$).

Trimargarin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{17}\text{H}_{33}\text{O})_3$ —848—has probably been obtained artificially as a crystalline solid, fusible at 60° ($140^\circ\text{F}.$), solidifiable at 52° ($125.6^\circ\text{F}.$). The substance formerly described under this name as a constituent of animal fats is a mixture of tripalmitin and tristearin.

Tristearin— $\text{C}_3\text{H}_5(\text{O}.\text{C}_{18}\text{H}_{35}\text{O})_3$ —890—is the most abundant constituent of the solid fatty substances. It is prepared in large quantities as an industrial product in the manufacture of stearin candles, etc., but is obtained free from tripalmitin only with great difficulty.

In as pure a form as readily obtainable, it forms a hard, brittle, crystalline mass; fusible at 68° ($154.4^\circ\text{F}.$), solidifiable at 61° ($141.8^\circ\text{F}.$); soluble in boiling alcohol, almost insoluble in cold alcohol, readily soluble in ether.

Triolein— $\text{C}_3\text{H}_5(\text{O.C}_{18}\text{H}_{33}\text{O})_3$ —884—exists in varying quantity in all fats, and is the predominant constituent of those which are liquid at ordinary temperatures. It may be obtained from animal fats by boiling with alcohol, filtering the solution, decanting after twenty-four hours' standing; freezing at 0° (32° F.), and expressing.

It is a colorless, odorless, tasteless oil; soluble in alcohol and ether, insoluble in water; sp. gr. 0.92.

The **Neutral Oils and Fats** are mixtures in varying proportions of the triglycerids of the acids of the acetic and acrylic series, principally tripalmitin, tristearin, and triolein. The first two of these are solid at the ordinary temperature and the last liquid. In the oils the last predominates, in the fats the former. In the cold the oils become solid (fats), and, on heating, the fats become oils. The fats and oils are usually odorless, white or yellow, unctuous to the touch, and produce a translucent stain upon paper. They are insoluble in and lighter than water, readily soluble in ether, petroleum ether, benzene, and many other organic solvents. Although the oils do not mix with water, and promptly rise to its surface after having been agitated with it, an oil may remain suspended for a long time; suspended in very minute globules in an aqueous liquid, if bile, pancreatin, albumen, or other **emulsifying agents** be present. Such a mixture, sometimes practically permanent, is called an **emulsion**.

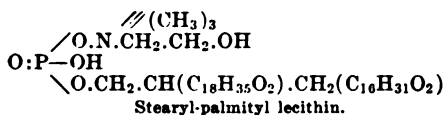
Like other esters the fats and oils are hydrolyzed or saponified when heated with steam or with a caustic alkali. The alcohol, glycerol, is liberated, and, if steam be used, the fatty acid also; while if an alkali be used a **soap** is formed, which is a salt of the fatty acid. The sodium soaps are hard, those of potassium soft. Castile soap is a sodium soap, made from olive oil. Yellow soap is made from tallow or other animal fat, and contains about one-third of its weight of rosin. Lead plaster is lead soap.

The **fixed oils** are so called to distinguish them from the **volatile oils**, more properly called **essences**, which are also unctuous to the touch, and render paper translucent, but which are hydrocarbons, not esters.

The vegetable oils form three classes: (1) The **non-drying, or greasy oils**, which remain liquid and greasy on exposure to air. Olive oil and peanut oil are representatives of this class. (2) **Drying oils**, which dry and become hard when exposed to air. These oils, which contain linoleic acid (p. 430), are used in making paints. Linseed, hemp, poppy, and sunflower oils are drying oils. (3) **Semi-drying oils** are intermediate between the other two classes, and are more or less drying. In this class are cottonseed, sesame, rape seed, and castor oils. The animal oils, used for dressing leather, as lubricants and for illumination, are fish oils, whale, and porpoise oil,

neat's foot oil, lard oil, and tallow oil. Cod liver oil contains, besides the glycerids of oleic, myristic, palmitic, and stearic acids, small quantities of those of butyric and acetic acids. It also contains certain biliary principles, a phosphorized fat, traces of iodine and bromine, probably in organic combination, a peculiar fatty acid called **gadinic acid**, a brown substance called **gadinin**, and two alkaloidal bodies: **asellin**, $C_{25}H_{32}N_4$, and **morrhuin**, $C_{19}H_{27}N_3$. **Sperm oil** is not a true oil, but a liquid wax; it contains no glycerids, but consists mainly of esters of the higher monoatomic alcohols.

Lecithins — Phosphorized Fats.—These substances are widely distributed in animal and vegetable tissues and fluids, and are particularly abundant in the yolks of eggs, brain, and nerve tissue, semen, and blood-corpuscles and plasma, where they probably serve as material for the formation of the more complex phosphorized bodies such as **protagon** and the **nucleins**. The lecithins are colorless or yellowish, imperfectly crystalline solids, of a waxy consistency, and very hygroscopic. They do not dissolve in water, but swell up in it like starch. They are soluble in chloroform, in benzene, and in hot alcohol and hot ether. From alcoholic solutions they crystallize in fine needles. When heated with baryta water or with acids they are decomposed into glycerophosphoric acid (p. 365), **cholin** (p. 383), and a fatty acid, usually palmitic or stearic. The lecithins are therefore derivatives of glycerophosphoric acid, in which the two remaining hydroxyls of the glycerol are replaced by fatty acid residues, and one of the two remaining basic hydrogen atoms of the phosphoric acid is replaced by the basic radical of **cholin**, which is a quaternary ammonium:



From the above formula it will be seen that the lecithins may unite with acids, through the remaining OH of the **cholin**, or with bases, through the remaining basic H of the phosphoric acid, to form salts. The lecithins differ from each other in the nature of the fatty acids entering into their composition. **Distearyl-**, **dioleyl-** and **stearyl-palmityl lecithins** are known.

ESTERS OF POLYHYDRIC ALCOHOLS, AND OF ALDO- AND KETO-ALCOHOLS

The superior alcohols form esters with the pure acids in the same manner as does glycerol. **Tetra-acetyl erythrol**: $C_4H_6(\text{C}_2\text{H}_3\text{O}_2)_4$, **Tetra-nitro erythrol**: $C_4H_6(\text{NO}_3)_4$; **Hexacetyl mannitol**: C_6H_8 .

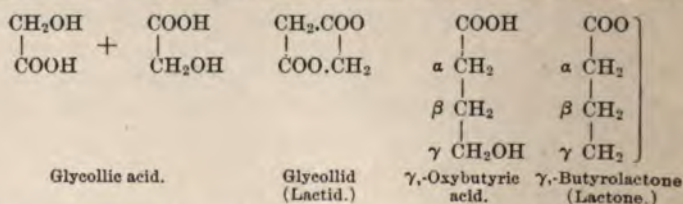
(C₂H₃O₂)₆, and **Hexanitro mannitol**: C₆H₈(NO₃)₆ are examples of such compounds.

The hexoses also form esters with mineral and organic acids. Thus **diacetic glucose**, C₆H₁₀O₄(CO₂.CH₃)₂, is formed as a very bitter solid, very soluble in water, alcohol and ether, by the action of acetic anhydrid upon glucose. This, heated with acetic anhydrid at 140°, furnishes **triacetic glucose**, C₆H₉O₃(CO₂.CH₃)₃, which, in turn, is converted into **tetracetic glucose**, C₆H₈O₂(CO₂.CH₃)₄, by the action of acetic anhydrid at 160°.

Acetochlorhydrate—CHO.(CH.CO₂.CH₃)₄.CH₂Cl—is formed by heating d-glucose with acetyl chlorid: C₆H₁₂O₆+4C₂H₃O.Cl=C₁₄H₁₉O₉Cl+3HCl+H₂O. It is a colorless, odorless, bitter semi-solid, insoluble in water, soluble in alcohol and in ether. It reduces Fehling's solution. Heated in presence of water, it regenerates glucose. Heated with potassium phenate, it forms glucosyl phenate, or phenol-glucosid, CHO.(CH.CO₂.CH₃)₄.CH₂Cl+C₆H₅.O.K.+4H₂O=CHO.(CHOH)₄CH₂.O.C₆H₅+KCl+4CH₃.COOH, the simplest of the **glucosids**, substances frequently referred to as esters of glucose, but which are more properly composite ethers containing glucose and phenolic residues, united by oxygen (p. 465).

ESTERS OF OXYACIDS—LACTIDS AND LACTONES.

The oxyacids not only form esters with the alcohols in the same manner as the pure acids, but, being themselves both alcohol and acid, they produce cyclic esters, in the formation of which they play the part of alcohol as well as that of acid. The **lactids** are formed by the interaction of two oxyacid molecules, each performing the functions of both alcohol and acid. The **lactones**, which are formed only by the γ and higher oxyacids, are produced from a single molecule of the acid, whose carboxyl and alcoholic groups interact with each other. The following formulæ will indicate the genesis of the lactids and lactones:



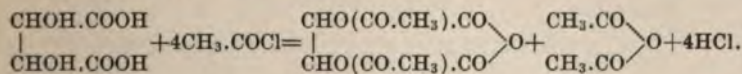
The γ lactones are formed from the γ monohalogen acids: (1) by distillation: COOH.CH₂.CH₂.CH₂Cl=COO.CH₂.CH₂.CH₂+HCl; (2) by boiling with H₂O, KHO or K₂CO₃: COOH.CH₂.CH₂.CH₂Cl+KHO=H₂O+KCl+COO.CH₂.CH₂.CH₂.

By reduction the higher lactones yield aldo-hexoses. Thus d-glucose is produced by the reduction of the lactone of d-gluconic acid:

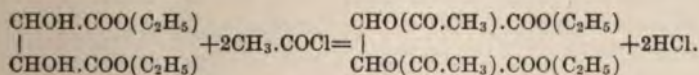
$\overline{\text{COO} \cdot (\text{CHOH})_4 \cdot \text{CH}_2} + \text{H}_2 = \text{CHO} \cdot (\text{CHOH})_4 \cdot \text{CH}_2\text{OH}$. The higher oxy-carboxylic acids readily lose water and are converted into lactones (p. 343).

Acylation—Determination of Hydroxyl, etc.—The formation of esters by the introduction of acidyls, referred to as **acylation**, is utilized to determine the number of alcoholic or phenolic (p. 443) hydroxyls contained in a molecule. The acidyls usually resorted to for this purpose are acetyl, CH_3CO , and benzoyl (pp. 456, 468), $\text{C}_6\text{H}_5\text{CO}$; and the reactions most frequently employed are those between the substance examined and the oxid or chlorid of the acidyl. Thus morphin, which contains two hydroxyls, one alcoholic and one phenolic, and acetic anhydrid produce diacetyl-morphin: $\text{C}_{17}\text{H}_{17}\text{NO}(\text{OH})_2 + (\text{CH}_3\text{CO})_2\text{O} = \text{C}_{17}\text{H}_{17}\text{NO}(\text{O} \cdot \text{OC} \cdot \text{CH}_3)_2 + \text{H}_2\text{O}$; phenol and acetyl chlorid produce phenyl acetate: $\text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{COCl} = \text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{OC} \cdot \text{CH}_3 + \text{HCl}$; and methyl alcohol and benzoyl chlorid produce methyl benzoate: $\text{H} \cdot \text{CH}_2\text{OH} + \text{C}_6\text{H}_5\text{COCl} = \text{C}_6\text{H}_5\text{COO}(\text{CH}_3) + \text{HCl}$. The H_2O produced when the anhydrid (or acid) is used, and the HCl with the chlorid, interfere with the completeness of the reaction (see below), and to remove them the operation is conducted in the presence of anhydrous sodium acetate in the former case, and of an alkali or pyridin (p. 518) in the latter. In some instances where the formation of H_2O or HCl must be avoided, and that of SH_2 is immaterial, thioacetic acid, CH_3COSH , is used to "acetylizize."

Certain precautions are necessary in applying acylation. The H of the groups NH , NH_2 and SH are also replaceable by acidyls (see diamins, p. 385), hence if present they must be taken into account. In some instances secondary reactions intervene. Thus tartaric acid, although containing four hydroxyls, only two of which are, however, non-carboxylic, takes up four molecules of acetyl chlorid, because of the secondary dehydrating action of the latter: $2\text{CH}_3\text{COCl} + \text{H}_2\text{O} = \text{CH}_3\text{CO})_2\text{O} + 2\text{HCl}$, and diacetyl tartaric anhydrid is formed:



This may be avoided by "protecting" the labile groups. Thus di-acetyl tartaric ester is formed, and only two molecules of acetyl chlorid enter into the reaction, if tartaric esters be used in place of the free acid:



The process of **alkylation**, i. e., the replacement of H in OH by alkyls to form esters, has more limited application. Alkyls may replace the H of OH in carboxyl COOH, in the methoxyl group of the primary alcohols, CH₂OH, and in the phenolic hydroxyl, C₆H₅.OH, but not in the secondary and tertiary alcoholic groups CHOH and COH. Therefore, alkylation may sometimes be resorted to to differentiate the latter hydroxyls from the former.

Sometimes direct esterification of alcohol and acid may serve to determine carboxylic hydroxyl in the absence of methoxyl or phenolic hydroxyl. But as this reaction is a reversible one, and is therefore not complete (p. 89), it can only be resorted to when means are adopted to remove one of the products and thus prevent the establishment of equilibrium until the reaction is completed. Usually it is the water which is removed by dehydrating agents such as KHSO₄. Thus the reaction between tartaric acid and ethyl alcohol: COOH.(CHOH)₂COOH + 2CH₃.CH₂OH $\rightleftharpoons$ COO(C₂H₅). (CHOH)₂.COO(C₂H₅) + 2H₂O may be made to progress from left to right by removing the water formed, by passing a current of dry HCl through an alcoholic solution of the acid. Or the formation of water may be avoided by using a salt of the acid whose cation forms an insoluble compound with a halogen, and a haloid ester. Thus with silver formate and methyl iodid: H.COOAg + CH₃I = H.COO(CH₃) + AgI.

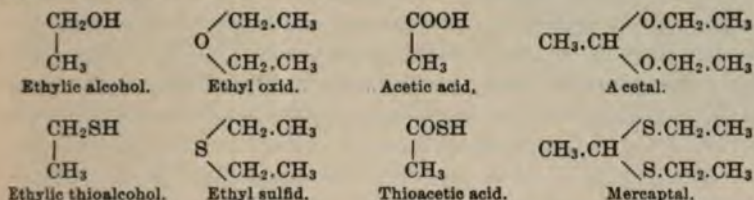
Phenolic hydroxyl may be distinguished from that of carboxyl by the fact that the esters produced by the latter are readily hydrolyzed by alkalis, but the phenolic esters are not. The alkyls of alkyl halids not only readily replace the hydrogen of NH, NH₂, and SH, but may, in aromatic compounds, become directly linked to carbon.

The number of carboxyls in an acid, its basicity, may be determined either by the electric conductivity of solutions of its sodium salt (p. 75), or by determination of its molecular weight and the percentage of metal in its salts, usually the silver salt, or by titration with normal alkali.

SULFUR DERIVATIVES OF THE PARAFFINS

As the mineral sulfids and sulfhydrates correspond to the oxids and hydroxids, so there exist **thioethers** and **thioalcohols**, which are the counterparts of the simple ethers and of the alcohols, as well as **thioaldehydes**, **thioketones** and **thioacids**. Moreover, as sulfur may be quadrivalent or hexavalent, as well as bivalent, there exist other important compounds, the **sulfoxids**, **sulfones** and **sulfonic acids**, which have no oxygen analogues.

The following formulæ will serve to illustrate the relations of the oxygen and thio compounds:

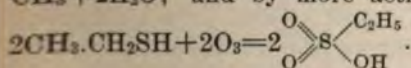


Thioethers, or Sulfids—are produced by processes corresponding to those by which the ethers are formed: (1) by distilling salts of ethyl-sulfuric acids with potassium sulfid: $2\text{KSO}_4.\text{C}_2\text{H}_5 + \text{K}_2\text{S} = \text{S}(\text{C}_2\text{H}_5)_2 + 2\text{K}_2\text{SO}_4$; (2) by the action of alkyl halids upon potassium sulfid: $2\text{CH}_3\text{Cl} + \text{K}_2\text{S} = \text{S}(\text{CH}_3)_2 + 2\text{KCl}$; (3) by the action of phosphorus pentasulfid upon the oxygen ethers: $4\text{O}(\text{C}_2\text{H}_5)_2 + \text{P}_2\text{S}_5 = \text{S}(\text{C}_2\text{H}_5)_2 + 2(\text{C}_2\text{H}_5)_3\text{PO}_2\text{S}_2$. The last is a general method by which the thio compounds may be obtained from the corresponding oxygen compounds, the secondary products being **thiophosphoric esters**.

The thioethers are colorless liquids, insoluble in water, soluble in alcohol and ether, of disagreeable odors. They contrast with the oxygen ethers chiefly in their additive power, dependent upon the greater valence capacity of sulfur. Thus they combine with alkyl iodids to form **sulfine iodids, or sulfonium iodids**, in which the sulfur is quadrivalent: $\text{S}(\text{C}_2\text{H}_5)_2 + \text{C}_2\text{H}_5\text{I} = \text{IS}(\text{C}_2\text{H}_5)_3$; and on oxidation they yield sulfoxids and sulfones, in which the sulfur is quadrivalent and hexavalent.

Thioalcohols—Mercaptans—are formed: (1) by the action of potassium sulfhydrate upon alkyl halids: $\text{KHS} + \text{CH}_3.\text{CH}_2\text{Cl} = \text{CH}_3.\text{CH}_2\text{SH} + \text{KCl}$; (2) by distilling the salts of the acid alkyl sulfates with potassium sulfhydrate: $\text{KSO}_4(\text{C}_2\text{H}_5) + \text{KHS} = \text{CH}_3.\text{CH}_2\text{SH} + \text{K}_2\text{SO}_4$; and (3) by the action of phosphorus pentasulfid upon the alcohol.

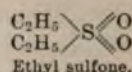
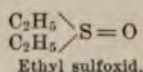
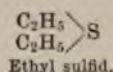
The thioalcohols differ in some of their general reactions from the alcohols: While the H of the OH of alcohols can only be replaced by K and Na among the metals, the H of SH may be replaced by the heavy metals as well. Thus with mercuric oxid: $2\text{CH}_3.\text{CH}_2\text{SH} + \text{HgO} = (\text{CH}_3.\text{CH}_2\text{S})_2\text{Hg} + \text{H}_2\text{O}$. Such metallic compounds are called **mercaptids**, and the name "mercaptan" (*mercurium captans*), is due to the formation of mercury mercaptid. Owing to the greater valence capacity of sulfur, the thioalcohols do not yield thioaldehydes and thioacids on oxidation. By limited oxidation mercaptans, or **mercaptids**, form **disulfids**: $4\text{CH}_3.\text{CH}_2\text{OH} + \text{O}_2 = 2\text{CH}_3.\text{CH}_2.\text{S}.\text{S}.\text{CH}_2.\text{CH}_3 + 2\text{H}_2\text{O}$; and by more active oxidation alkyl sulfonic acids:



Ethyl mercaptan—**Ethyl sulfhydrate**—**Thioalcohol**— $\text{CH}_3\text{CH}_2\text{SH}$ —is prepared industrially, as the first step in the formation of sulfonal, by the first of the general methods given above. It is a colorless liquid, sp. gr. 0.8325, boils at 36.2° (97.2° F.), has an intensely disagreeable odor, burns with a blue flame, is neutral in reaction, sparingly soluble in water, soluble in alcohol and in ether, dissolves I, S and P. Potassium and sodium act upon mercaptan as they do upon alcohol, replacing the extra-radical hydrogen to produce **mercaptids**, or **thioethylates**, corresponding to the ethylates.

There also exist **mono-** and **di-thioglycols**, corresponding to the dihydric alcohols (p. 294). One of these, **monothioethylene glycol**: $\text{C}_2\text{H}_4\text{OH.SH}$, yields isethionic acid on oxidation (see below).

Sulfoxids and **Sulfones**—are products of oxidation of the sulfids, in which the sulfur is quadrivalent or hexavalent:



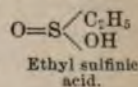
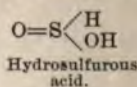
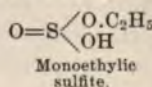
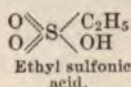
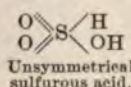
Other products of oxidation of thio-compounds, containing the group $(\text{SO}_2)''$ attached to a hydrocarbon group, are also called **sulfones** (see below).

Sulfonic Acids—are acids containing the group $(\text{O}_2\text{S.OH})'$ attached to a hydrocarbon group. The sulfonic acids of this series are formed by oxidation of the mercaptans; by the action of the paraffin iodids upon the alkaline sulfites; or by the action of sulfuric acid upon alcohols, ethers, etc. (see Aromatic Sulfonic Acids). They may be considered as being derived from the unsymmetrical sulfurous acid (p. 144) by replacement of the H atom by an alkyl; and are isomeric with the monoalkyl sulfites (formula below), from which they are distinguished by the fact that the latter, being esters, are saponified by alkalies, which the former are not.

The thioglycols on oxidation also yield sulfonic acids. **Isethionic acid**, $\text{C}_2\text{H}_4\text{OH.SO}_3\text{H}$, mentioned above, is a thick liquid, whose amido derivative is **taurin** (see Amido-acids).

In the **thiosulfonic acids**, which only exist in their salts and esters, the oxygen in the hydroxyl of the sulfonic acids is replaced by sulfur.

Sulfinic acids bear the same relation to hydrosulfurous acid that the sulfonic acids do to the unsymmetrical sulfurous acid:

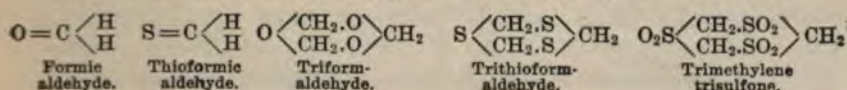


Thioaldehydes and their Sulfones.—The simple thioaldehydes are not known, owing to the tendency to polymerize which they pos-

sess to a still more marked degree than the aldehydes (p. 300). The trithioaldehydes and their sulfones are odorless, colorless solids.

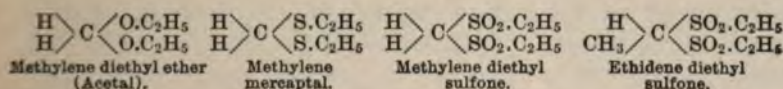
Trithioformaldehyde, or **parathioformaldehyde**, crystallizes in needles, insoluble in water, f. p. 216° , and forms crystalline compounds with AgNO_3 and PtCl_4 . It is produced: (1) by the action of nascent H upon carbon bisulfid: $3\text{CS}_2 + 6\text{H}_2 = (\text{CH}_2\text{S})_3 + 3\text{SH}_2$; (2) by heating methylene diiodid with Na_2S : $3\text{CH}_2\text{I}_2 + 3\text{Na}_2\text{S} = (\text{CH}_2\text{S})_3 + 6\text{NaI}$; (3) by the action of H_2S on formic aldehyde: $3\text{H}.\text{CHO} + 3\text{H}_2\text{S} = (\text{CH}_2\text{S})_3 + 3\text{H}_2\text{O}$; (4) by the reduction of thiocyanic acid: $3\text{CNSH} + 6\text{H}_2 = (\text{CH}_2\text{S})_3 + 3\text{NH}_3$.

The relations of these compounds are shown by the formulæ:



In trimethylene trisulfone the SO_2 groups influence the included CH_2 groups in the same manner as do the CO groups in the ketonic and malonic esters (p. 361); their H atoms are similarly replaceable by Na, and this by alkyls.

Thioacetals—Mercaptals—are produced by the action of paraffin iodids upon alkali mercaptids, or by the action of HCl upon a mixture of aldehyde and mercaptan. By oxidation they yield sulfones, whose methylene hydrogen may be replaced by alkyl groups:



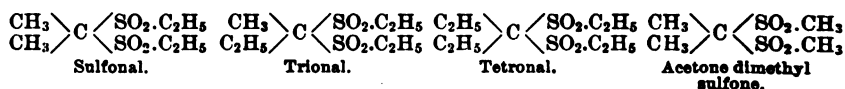
Thioketones.—The simple thioketones, $(\text{CH}_3)_2:\text{CS}$, corresponding to the acetones, $(\text{CH}_3)_2:\text{CO}$, are not known. But, when P_2S_5 acts upon acetone, **dithioketone**, $(\text{CH}_3)_2:\text{C} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{C}:(\text{CH}_3)_2$ is produced as a yellow liquid, b. p. 184° , which is reduced by nascent hydrogen to isopropyl mercaptan: $(\text{CH}_3)_2:\text{CH}.\text{SH}$. By the action of H_2S upon a mixture of acetone and HCl, **trithioacetone**, $(\text{CH}_3)_2 \begin{array}{c} \text{S.C}(\text{CH}_3)_2 \\ \diagup \quad \diagdown \\ \text{S.C}(\text{CH}_3)_2 \end{array} \text{S}$, is produced.

Mercaptols and their Sulfones.—The mercaptols are substances which may be considered as derived from the ketones by substitution of two thioalkyl groups for the oxygen. Thus **acetone-ethyl mercaptol**, or **dithioethyl-dimethyl methane**, $\text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array} \begin{array}{c} \text{S.C}_2\text{H}_5 \\ \diagup \quad \diagdown \\ \text{S.C}_2\text{H}_5 \end{array}$, is derivable from acetone, $\text{CH}_3.\text{CO}.\text{CH}_3$. They are formed by the action of HCl upon a mixture of acetone and mercaptan: $\text{CH}_3.\text{CO}.\text{CH}_3 + 2\text{CH}_3.\text{CH}_2\text{SH} = (\text{CH}_3)_2:\text{C}:(\text{S}.\text{C}_2\text{H}_5)_2 + \text{H}_2\text{O}$. Or sodium ethylthiosulfate, which is decomposed by mineral acids, with formation of mercaptan: $\text{C}_2\text{H}_5\text{S}.$

$\text{SO}_3\text{Na} + \text{H}_2\text{O} = \text{NaHSO}_4 + \text{CH}_3.\text{CH}_2\text{SH}$, may be used in place of the thioalcohol. Ethyl mercaptol is a mobile liquid, of not unpleasant odor, b. p. 190° , manufactured as a step in the production of sulfonal. The sulfones are obtained from the mercaptols by oxidation.

Sulfonal—Acetone Diethyl Sulfone—Disulfethyl-dimethyl methane $-(\text{CH}_3)_2:\text{C}:(\text{SO}_2\text{C}_2\text{H}_5)_2$ —is obtained by oxidizing ethyl mercaptol by potassium permanganate. It crystallizes in thick, colorless prisms, difficultly soluble in cold water or alcohol, readily soluble in hot water or alcohol, and in ether, benzene and chloroform. It fuses at 126° (226.8°F.) and boils at 300° (572°F.), suffering partial decomposition.

Sulfonal contains two ethyl groups, **trional** contains three, and **tetronal** four. Their hypnotic power increases with the number of ethyl groups which they contain. Other "sulfonals" are obtainable from the corresponding mercaptols by methods similar to the above. Among these is **acetone dimethyl sulfone**, which contains no ethyl group, and has no hypnotic action. The relations of these compounds is shown by the following formulæ :



Ichthyol.—is the Na salt of a complex sulfonic acid, having the empirical formula $\text{C}_{28}\text{H}_{36}\text{S}_3\text{O}_6\text{Na}_2$, obtained by the distillation and purification of an ozocerite (a mineral pitch). It is a dark brown, pitchlike mass, having a disagreeable odor, soluble in water and in glycerol.

Thioacids and their Thioanhydrids.—In the thioacids of the acetic series the sulfur is substituted for the oxygen in the hydroxyl. **Thioacetic acid**, $\text{CH}_3.\text{CO}.\text{SH}$, is formed by the action of phosphorus pentasulfid upon acetic acid.

Thiolactic Acid— $\text{CH}_3.\text{CHSH}.\text{COOH}$ —is formed by the continued heating of ethyl- α -chloropropionate with potassium hydrosulfid, and decomposition of the ester: $\text{CH}_3.\text{CHCl}.\text{COO}(\text{C}_2\text{H}_5) + \text{KHS} + \text{H}_2\text{O} = \text{CH}_3.\text{CHSH}.\text{COOH} + \text{CH}_3.\text{CH}_2\text{OH} + \text{KCl}$. It crystallizes in needles, f. p. 142° . It and the β acid: $\text{CH}_2\text{SH}.\text{CH}_2.\text{COOH}$ are of interest in connection with cystin (p. 421).

Thioacids derivable from Carbonic acid.—Five of these compounds are known in their derivatives, although the free acids are unknown, or very unstable. The formulæ of the free acids are: $\text{CO} \begin{array}{c} \text{SH} \\ \text{OH} \end{array}$, $\text{CO} \begin{array}{c} \text{SH} \\ \text{SH} \end{array}$, $\text{CS} \begin{array}{c} \text{OH} \\ \text{OH} \end{array}$, $\text{CS} \begin{array}{c} \text{SH} \\ \text{OH} \end{array}$, and $\text{CS} \begin{array}{c} \text{SH} \\ \text{SH} \end{array}$.

Carbon Disulfid— CS_2 —bears the same relation to sulfothiocarbonic acid, $\text{CS} \begin{array}{c} \text{SH} \\ \text{OH} \end{array}$, and to trithiocarbonic acid, $\text{CS} \begin{array}{c} \text{SH} \\ \text{SH} \end{array}$, that carbon dioxid bears to carbonic acid (p. 340). It is prepared by passing

vapor of S over C heated to redness, is partly purified by rectification, and obtained pure by redistillation over mercuric chlorid.

It is a colorless liquid. When pure it has a peculiar, but not disagreeable odor, the nauseating odor of the commercial product being due to the presence of another sulfurated body; boils at 47° (116.6° F.); sp. gr. 1.293; very volatile. Its rapid evaporation in vacuo produces a cold of -60° (-76° F.). It does not mix with H_2O . It refracts light strongly.

It is highly inflammable, and burns with a bluish flame, giving off CO_2 and SO_2 ; its vapor forms highly explosive mixtures with air, which detonate on contact with a glass rod heated to 250° (482° F.). Its vapor forms a mixture with nitrogen dioxid, which, when ignited, burns with a brilliant flame, rich in actinic rays.

A substance also exists, intermediate in composition between CO_2 and CS_2 , known as **carbon oxysulfid**, CSO , which is an inflammable, colorless gas, obtained by decomposing potassium thiocyanate with dilute H_2SO_4 .

Toxicology.—Workmen engaged in the manufacture of CS_2 , and in the vulcanization of rubber, as well as others exposed to the vapor of the disulfid, are subject to a form of chronic poisoning which may be divided into two stages. The first, or stage of excitation, is marked by headache, vertigo, a disagreeable taste, and cramps in the legs. The patient talks, laughs, sings, and weeps immoderately, and sometimes becomes violently delirious. In the second stage the patient becomes sad and sleepy, sensibility diminishes, sometimes to the extent of complete anæsthesia, especially of the lower extremities, the headache becomes more intense, the appetite is greatly impaired, and there is general weakness of the limbs, which terminates in paralysis.

ORGANO-METALLIC COMPOUNDS.

These are compounds of organic radicals with metallic elements, the best known being those of the alkyls with zinc and mercury.

Zinc-methyl, or **Zinc Methid**— $(CH_3)_2Zn$, and **Zinc-ethyl**, or **Zinc Ethid**— $(C_2H_5)_2Zn$ —are formed by heating to 130° – 150° methyl or ethyl iodid with excess of zinc amalgam, and distilling without contact of air. They are colorless liquids, the former b. p. 46° , sp. gr. 1.386, the latter b. p. 118° , sp. gr. 1.182. On contact of air they ignite and burn, giving off dense clouds of ZnO . By the moderated action of air they produce solid oxyalkylates: $Zn \begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{O.CH}_3 \end{smallmatrix}$, or alcoholates: $Zn \begin{smallmatrix} \text{O.CH}_3 \\ \diagup \\ \text{O.CH}_3 \end{smallmatrix}$. The former are also produced, along with hydrocarbons, by the action of zinc-alkyls upon alcohols: $(CH_3)_2Zn +$

$\text{H}.\text{CH}_2\text{OH}=\text{CH}_3.\text{O}.\text{Zn}.\text{CH}_3+\text{CH}_4$; and are decomposed by water with formation of hydrocarbons and primary alcohols: $\text{CH}_3.\text{O}.\text{Zn}.\text{CH}_3+2\text{H}_2\text{O}=\text{ZnH}_2\text{O}_2+\text{H}.\text{CH}_2\text{OH}+\text{CH}_4$. With the halogens the zinc alkyls react violently to form alkyl halids: $(\text{CH}_3)_2\text{Zn}+2\text{Br}_2=2\text{CH}_3\text{Br}+\text{ZnBr}_2$. They unite with sulfur dioxide to produce zinc alkyl-sulfates (p. 372): $(\text{C}_2\text{H}_5)_2\text{Zn}+\text{SO}_2=(\text{O}:\text{S}\begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{O} \end{smallmatrix})_2\text{Zn}$. With acidyl chlorids and aldehydes they form complex compounds, which are decomposed by water to form ketones, or tertiary or secondary alcohols.

NITROGEN DERIVATIVES OF THE PARAFFINS.

Speaking strictly, the only nitrogen derivatives of the paraffins are the nitrils, derived from the paraffins by substitution of N for H₃, as $\text{CH}_3.\text{CN}$, from $\text{CH}_3.\text{CH}_3$ and the diazo paraffins, $(\text{N}_2)''\text{CH}.\text{CH}_3$, but the compounds derivable from the paraffins and from their oxidation products by substitution of nitrogen containing groups, NO_2 , NO , NH_2 , NH , NOH , —N:N— , and =N.N= , are numerous, varied and important.

NITROPARAFFINS.

The univalent group (NO_2) is designated by the syllable **nitro** in the names of compounds containing it.

The **mononitroparaffins**—isomeric with the nitrous esters (p. 359), are derived from the paraffins by the substitution of NO_2 for an atom of hydrogen, and are distinguished as *primary*, *secondary* and *tertiary*, in the same manner as the corresponding alcohols (p. 283) according as the NO_2 is united to CH_2 , or CH , or C . They are formed by the action of the alkyl iodids upon silver nitrite: $\text{CH}_3\text{I}+\text{AgNO}_2=\text{AgI}+\text{CH}_3\text{NO}_2$.

They are isomeric with the nitrous esters: $\text{CH}_3.\text{CH}_2.\text{N}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}=\text{mononitroethane}$, and $\text{CH}_3.\text{CH}_2.\text{ON}:\text{O}=\text{Ethyl nitrite}$. These isomeres may be distinguished by the action of KHO , which saponifies the esters: $\text{C}_2\text{H}_5.\text{ON}:\text{O}+\text{KHO}=\text{KON}:\text{O}+\text{CH}_3.\text{CH}_2\text{OH}$, but has no action upon the nitroparaffins.

Nascent hydrogen converts them first into hydroxylamin compounds (p. 152): $\text{CH}_3.\text{NO}_2+2\text{H}_2=\text{CH}_3.\text{NH}.\text{OH}+\text{H}_2\text{O}$, which are in turn further reduced to monamins, or amidoparaffins: $\text{CH}_3.\text{NH}.\text{OH}+\text{H}_2=\text{NH}_2.\text{CH}_3+\text{H}_2\text{O}$.

Nitrous acid converts the primary nitroparaffins into **nitrolic acids**, as **ethyl-nitrolic acid**, $\text{CH}_3.\text{C}\begin{smallmatrix} \text{NO}_2 \\ \text{NOH} \end{smallmatrix}$, the liquid assuming a red color. The same agent converts the secondary nitroparaffins into **pseudonitrols**, as **propyl pseudonitrol**, $\text{CH}_3\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}\text{C}\begin{smallmatrix} \text{NO}_2 \\ \text{NO} \end{smallmatrix}$, the liquid be-

coming blue. Upon the tertiary nitroparaffins nitrous acid has no action. These reactions are utilized to distinguish primary, secondary, and tertiary alcohols from each other. The alcohol is first converted into an iodid, which is then distilled with AgNO_2 . The distillate is then treated with KHO and KNO_2 , and dilute H_2SO_4 is added.

AMINS AND AMMONIUM DERIVATIVES.

The amins are compounds derived from ammonia by the substitution of alkyls for a part or all of its hydrogen.

They are classified into **monamins**, derived from a single molecule of ammonia, **diamins**, derived from two such molecules, and **triamins**, derived from three.

MONAMINS AND THEIR DERIVATIVES.

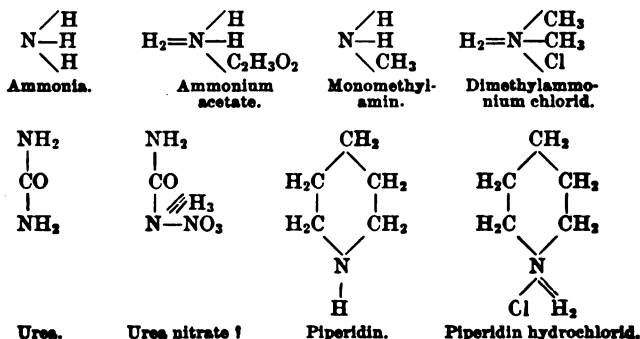
The monamins are **primary**, **secondary**, or **tertiary**, as one, two, or three of the hydrogen atoms of ammonia have been replaced. They are also distinguished as **amin**, **imin**, and **nitril bases**. When, in secondary or tertiary amins, the substituted radicals are alike the amins are designated as **simple**, when the radicals are different the amins are **mixed**. The primary monamins, containing the group NH_2 , are **amido-paraffins**; while the secondary, containing the group NH , are **imido-paraffins**. The monamins have the algebraic formula, $\text{NC}_n\text{H}_{2n+3}$.

A nomenclature similar to the above is also used in speaking of nitrogen in other, more complex, organic compounds. It is said to be in **primary combination**, or as **amid**, or **amin nitrogen**, when in the **amido**, or **amino group** $(\text{NH}_2)'$, in **secondary combination**, or as **imid**, or **imin nitrogen**, when in the **imido**, or **imin, group** $(\text{NH})''$, and in **tertiary combination**, or as **nitril nitrogen**, when in the form N''' . **Azo-**, **diazo-**, and **hydrazo-** nitrogen is in the forms $-\text{N}:\text{N}-$ and $=\text{N}.\text{N}=\text{}$.

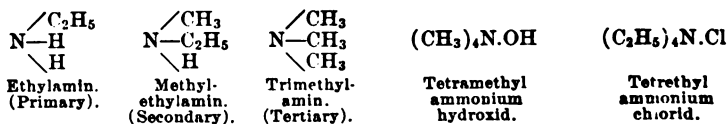
The monamins are sometimes called **compound ammonias**, from their resemblance to ammonia in their chemical properties, as well as from their origin. They combine with water to produce **quarternary ammonium hydroxids**, similar in constitution, alkalinity, and basicity to ammonium hydroxid; and with acids, without elimination of hydrogen, to form salts, similar to the ammoniacal salts.

The aliphatic monamins are the most simply constituted of a great variety of nitrogen derivatives, including the primary monamids (p. 399), the diamids, such as urea, and the vegetable alkaloids (p. 545), which have this in common with the amins, that they are basic in char-

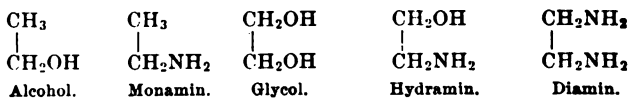
acter, and, in combining with acids, form salts in the same manner as ammonia does, i. e., by change of the nitrogen valence from three to five, and, consequently, without elimination of hydrogen. As the hydroxids and salts of such basic nitrogen-carbon compounds are addition products: $N'''(CH_3)_3 + H_2O = HO.N'''(CH_3)_3$, the bases themselves are in this sense unsaturated compounds (p. 269).



The naming of these compounds has been the subject of much discussion. As the substances formed by the union of ammonia with acids are regarded as salts of ammonium, not of ammonia, so these compounds are not salts of urea, piperidin, morphin, etc., but salts of hypothetical bases, containing a quinquivalent nitrogen atom, which in the free base is trivalent. The names: *ureium nitrate*, *piperidium chlorid*, *morphium sulfate*, etc., are therefore the analogues of *ammonium acetate* and *dimethylammonium chlorid*. For the chlorin, bromin, and iodine compounds the names: piperidin hydrochlorid, morphin hydrobromid, quinin hydroiodid, etc., may be conveniently retained, they being regarded as the free bases, plus hydrogen, plus the halogen. The following formulæ indicate the constitution of the amines and their hydroxids and salts:



The primary monamins, the hydramins, and the diamins (p. 385) may also be considered as derived from the monohydric and dihydric alcohols by substitution of NH_2 for OH . (See also p. 382):



The **primary monamins** are formed: (1) by distilling the isocyanic esters with caustic potash: $\text{CO:N.C}_2\text{H}_5 + 2\text{KHO} = \text{NH}_2.\text{C}_2\text{H}_5 + \text{CO}_3\text{K}_2$; (2) by heating the alkyl iodids, or the nitric esters, with alcoholic ammonia: $\text{C}_2\text{H}_5\text{I} + \text{NH}_3 = \text{NH}_2.\text{C}_2\text{H}_5 + \text{HI}$, or $\text{C}_2\text{H}_5.\text{NO}_3 + \text{NH}_3 = \text{NH}_2.\text{C}_2\text{H}_5 + \text{HNO}_3$; (3) by the action of nascent H in alcoholic solution upon the nitrils (p. 393): $\text{CH}_3.\text{CN} + 2\text{H}_2 = \text{NH}_2.\text{C}_2\text{H}_5$; (4) by the action of nascent H upon the nitroparaffins: $\text{CH}_3.\text{NO}_2 + 3\text{H}_2 = \text{NH}_2.\text{CH}_3 + 2\text{H}_2\text{O}$; (5) from the monamids (p. 400) of the fatty series monamins, containing one atom of carbon less than the amid, are formed by the action of bromin and potassium hydroxid. The reaction occurs in two stages. First a bromid is produced: $\text{C}_2\text{H}_5.\text{CO}.\text{NH}_2 + \text{Br}_2 + \text{KHO} = \text{C}_2\text{H}_5.\text{CO}.\text{NHBr} + \text{KBr} + \text{H}_2\text{O}$, which is in turn converted into the amin with loss of the carbonyl group: $\text{C}_2\text{H}_5.\text{CO}.\text{NHBr} + 3\text{KHO} = \text{C}_2\text{H}_5.\text{NH}_2 + \text{CO}_3\text{K}_2 + \text{H}_2\text{O} + \text{KBr}$; (6) by reduction of aldoxims and ketoxims (410).

The **secondary monamins** are formed, as intermediate products, by the action of the alkyl iodids upon the primary monamins in the presence of excess of ammonia. The alkyl-ammonium iodid is first produced: $\text{NH}_2.\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{I} = \text{NH}(\text{C}_2\text{H}_5)_2\text{HI}$, and this reacts with the ammonia: $\text{NH}(\text{C}_2\text{H}_5)_2\text{HI} + \text{NH}_3 = \text{NH}(\text{C}_2\text{H}_5)_2 + \text{NH}_4\text{I}$. The final products of the reaction are the tetrammonium iodids: $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$.

The **tertiary monamins** are obtained by the dry distillation of the quarternary ammonium hydroxids, iodids, or chlorids: $\text{N}(\text{C}_2\text{H}_5)_4\text{I} = \text{N}(\text{C}_2\text{H}_5)_3 + \text{C}_2\text{H}_5\text{I}$; or by heating the primary or secondary amins with excess of potassium alkyl sulfate: $\text{NH}(\text{CH}_3)_2 + \text{CH}_3\text{K}.\text{SO}_4 = \text{N}(\text{C}_2\text{H}_5)_3 + \text{KHSO}_4$.

The alkalinity and solubility in water of the primary monamins are greater than those of the secondary, and those of the secondary greater than those of the tertiary.

The primary and secondary amins react with esters of the mono-carboxylic acids to form alcohols and primary or secondary amids (p. 400). Thus methylamin and methyl acetate produce ethyl alcohol and acetamid: $\text{H}_2\text{N}.\text{CH}_3 + \text{CH}_3.\text{COO}(\text{CH}_3) = \text{CH}_3.\text{CH}_2\text{OH} + \text{H}_2\text{N}(\text{CO}.\text{CH}_3)$. With esters of dicarboxylic acids primary monamins produce mono- or dialkyl diamids (p. 406); secondary monamins produce esters of alkyl amic acids (p. 402), alcohols being formed in both cases; and tertiary monamins are not acted upon. Thus oxalic ester produces dimethyloxamid with methylamin, and dimethyloxamic ester with dimethylamin: $2\text{H}_2\text{N}.\text{CH}_3 + \text{COO}(\text{C}_2\text{H}_5).\text{COO}(\text{C}_2\text{H}_5) = \text{H}_3\text{C}.\text{HN}(\text{CO}.\text{CO}.\text{NH}.\text{CH}_3)_2 + 2\text{CH}_3.\text{CH}_2\text{OH}$, and $\text{HN}(\text{CH}_3)_2 + \text{COO}(\text{C}_2\text{H}_5).\text{COO}(\text{C}_2\text{H}_5) = (\text{CH}_3)_2\text{N}.\text{CO}.\text{COO}(\text{C}_2\text{H}_5) + \text{CH}_3.\text{CH}_2\text{OH}$. These last reactions are utilized in Hofmann's method of separating primary, secondary and tertiary amins, as the diamids produced are soluble in water, but the amic esters are not.

Formic aldehyde condenses with primary amines to form cyclic amines, with secondary amines to form alkyl diamines (p. 386), and has no action upon tertiary amines. As the boiling points of these products and of the tertiary amines differ widely, this reaction is also utilized to separate the amines. Formic aldehyde with methylamine produces trimethyl trimethylene-amine; and with dimethylamine, tetramethyl methylene diamine: $3\text{H}_2\text{NCH}_3 + 3\text{H}.\text{CHO} = \text{H}_2\text{C} \begin{smallmatrix} \text{N}(\text{CH}_3).\text{CH}_2 \\ \text{N}(\text{CH}_3).\text{CH}_2 \end{smallmatrix} \text{N}(\text{CH}_3) + 3\text{H}_2\text{O}$; and $2\text{HN}(\text{CH}_3)_2 + \text{H}.\text{CHO} = (\text{CH}_3)_2\text{N}.\text{CH}_2.\text{N}(\text{CH}_3)_2 + \text{H}_2\text{O}$.

More rapid methods of distinguishing nitril, imide and amid nitrogen in the amines, and other similar basic substances, are based upon their varying behavior with certain cyclic acidyls. Thus benzene sulfochloride, $\text{C}_6\text{H}_5.\text{SO}_2\text{Cl}$ (p. 469), in the presence of alkali has no action upon tertiary amines; with secondary amines it forms insoluble, oily or solid products, which precipitate; and with primary amines it produces phenylsulfoamides which remain in solution in the alkali, but are precipitated by addition of HCl as crystalline solids, having definite fusing points.

A slight elevation of temperature (to 50°) causes the decomposition of ammonium nitrite with evolution of free nitrogen: $(\text{NH}_4)\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O}$. Similarly nitrous acid and primary amines enter into double decomposition with liberation of the nitrogen of both, and formation of alcohols, either primary, secondary or tertiary: $\text{H}_2\text{N}.\text{CH}_3 + \text{HNO}_2 = \text{N}_2 + \text{H}.\text{CH}_2\text{OH} + \text{H}_2\text{O}$. This reaction is common to the **amido group**, NH_2 , in almost all aliphatic compounds, and the liberation of free nitrogen by the action of nitrous acid is utilized to detect the presence of this group in such compounds. The amido group in cyclic compounds behaves differently with nitrous acid, forming azo- or diazo compounds, containing the bivalent azo group $-\text{N}:\text{N}-$ (p. 481), and occasional instances of similar behavior with aliphatic compounds are met with, as in the formation of the azo-fatty acids: $(\text{N}:\text{N})\text{CH}.\text{COOH}$. Nitrous acid with the secondary amines, containing the **imido group**, NH , forms **nitroso amines**, containing the **nitroso group** (NO). Thus dimethylamine forms nitrosodimethylamine: $\text{HN}(\text{CH}_3)_2 + \text{HNO}_2 = \text{NO}.\text{N}(\text{CH}_3)_2 + \text{H}_2\text{O}$.

Or the existence of amido or imido groups and their number, in both aliphatic and cyclic compounds, may be determined by acylation or alkylation (p. 369), an amido group taking up two acidyls or alkyls, and an imido group but one.

The primary monamines, when warmed with chloroform and alcoholic potash, yield **carbylamines**, **isocyanides**, or **isonitrils** (p. 394): $\text{NH}_2.\text{C}_2\text{H}_5 + \text{CHCl}_3 + 3\text{KHO} = \text{CN}.\text{C}_2\text{H}_5 + 3\text{KCl} + 3\text{H}_2\text{O}$. (See Chloroform, test 1, p. 279.)

When ethereal solutions of primary monamines and of carbon disulfide are evaporated, a residue is obtained which, when heated in aqueous solution with AgNO_3 , or Fe_2Cl_6 , or HgCl_2 forms a sulfide of the

metal and a "mustard oil," having a pungent odor. This is Hoffman's test for primary monamins (see p. 379).

The hydrochlorids of the amins and of many other basic carbon-nitrogen compounds in which the nitrogen behaves as it does in ammonia in the formation of salts, also resemble ammonium chlorid in that they form crystalline, and, frequently, difficultly soluble chloroplatinates with PtCl_4 . Thus: methylamin chloroplatinate, $(\text{H}_3\text{C.N}^+\text{H}_3)_2\text{PtCl}_6$. These compounds, along with the crystalline chloraurates: $(\text{H}_3\text{C.NH}_3)\text{AuCl}_3$, and picrates: $(\text{H}_3\text{C.NH}_3)\text{O.C}_6\text{H}_2(\text{NO}_2)_3$, which are also formed by such carbon-nitrogen compounds, are largely utilized for their separation, identification and analysis.

There also exist amins of the type R'.N:R'' , such as methylene-methylamin: $\text{CH}_3.\text{N:CH}_2$, which are formed by the action of formic aldehyde upon the amins: $\text{CH}_3.\text{NH}_2 + \text{H.CHO} = \text{CH}_3.\text{N:CH}_2 + \text{H}_2\text{O}$. (See also diamins, p. 385.)

Methylamin—*Methylia*— $\text{H}_2\text{N.CH}_3$ —is a colorless, inflammable gas, having a fishy, ammoniacal odor. Very soluble in water (1,154 volumes in one at 12.5°), forming a highly caustic and alkaline solution. It neutralizes acids with formation of methyl ammonium salts, which are soluble in water. Its chloroplatinate crystallizes in yellow scales, soluble in water, insoluble in alcohol: its chloraurate in yellow needles, soluble in water, alcohol and ether.

Dimethylamin—*Dimethylia*— $\text{HN}(\text{CH}_3)_2$ —is a liquid below 7.2° , has an ammoniacal odor, and is very soluble in water. Its chloroplatinate forms yellow needles.

Trimethylamin—*Trimethylia*— $\text{N}(\text{CH}_3)_3$ —is formed by the action of methyl iodid upon NH_3 , and as a product of decomposition of many organic substances. It occurs naturally in combination in cod-liver oil, ergot, chenopodium, yeast, guano, and many flowers. It is an oily liquid below 9° , having a fishy odor, alkaline, soluble in water, alcohol and ether. Its chloroplatinate crystallizes in octahedra, insoluble in alcohol.

The three methylamins were first obtained from herring-pickle. They are formed as early products of putrefaction of fish, starch-paste, brain- and muscular tissue, and proteins, along with ethylamin and diethylamin. The commercial "trimethylamin" obtained by dry distillation of distillery waste, is a mixture of the three methylamins in about the proportions: 40, 50 and 10 per cent.

Ethylamin— $\text{H}_2\text{N.CH}_2.\text{CH}_3$ —is a mobile liquid, b. p. 18° , which expels ammonia from ammoniacal salts.

Propylamin— $\text{H}_2\text{N.CH}_2.\text{CH}_2.\text{CH}_3$ —is also a liquid, b. p. 49° , obtained from propionitril. The medicinal substance called *chlorid of secalia* is not this amin, but its isomere, trimethylamin.

Tetramethyl-ammonium Hydroxid— $\text{HO.N}(\text{CH}_3)_4$ —is a quarter-

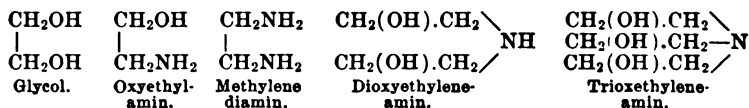
nary ammonium hydroxid, corresponding to ammonium hydroxid, and is obtained by decomposing the iodid, $\text{IN}(\text{CH}_3)_4$, which is formed by the action of methyl iodid upon trimethylamin. It is a crystalline, deliquescent, caustic solid, not volatile without decomposition. Like other carbon-nitrogen hydroxids and hydramins, it absorbs carbon dioxid from the air.

Tetrethyl-ammonium Hydroxid— $\text{HO.N}(\text{C}_2\text{H}_5)_4$ —forms strongly alkaline, deliquescent needles, and has been used as a solvent for uric acid.

There are also primary monamins corresponding to the secondary and tertiary alcohols (p. 283), which are monamins containing iso- or meso-alkyls (p. 274), and are called **carbinamins**. Those corresponding to the secondary alcohols are obtained (1) by reduction of the ketohydrazones (p. 410), (2) by reduction of the ketoxims (p. 410), and (3) by the action of β alkyl iodids upon ammonia. Thus **isopropylamin**, or **dimethylcarbinamin**, is obtained (1) from dimethylacetone hydrazone: $(\text{CH}_3)_2\text{C}:\text{N.NH.C}_6\text{H}_5 + 2\text{H}_2 = (\text{CH}_3)_2\text{CH.NH}_2 + \text{C}_6\text{H}_5\text{.NH}_2$; (2) from acetoxim: $(\text{CH}_3)_2\text{C}:\text{NOH} + 2\text{H}_2 = (\text{CH}_3)_2\text{CH.NH}_2 + \text{H}_2\text{O}$; and (3) from β iodopropane and ammonia: $\text{CH}_3\text{.CHI.CH}_3 + 2\text{NH}_3 = (\text{CH}_3)_2\text{CH.NH}_2 + \text{NH}_4\text{I}$.

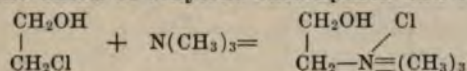
OXYAMINS (HYDRAMINS), DIAMINS, IMINS AND DIIMINS.

The primary monamins may be considered as being derived from the monoatomic alcohols by the substitution of the amido group, NH_2 , for the hydroxyl. From the dihydric alcohols, the glycols, two classes of amido compounds may be similarly derived. One of these, the **oxyamins**, **hydroxamins**, or **hydramins**, contain a single amido group, and retain an alcoholic hydroxyl. In the **diamins** both hydroxyls are replaced by amido groups. The oxyamins are primary, secondary and tertiary in the same manner as the monamins:



The primary oxyamins are produced: (1) by the action of ammonia upon the halohydrins: $\text{CH}_2\text{OH.CH}_2\text{Cl} + \text{NH}_3 = \text{CH}_2\text{OH.CH}_2\text{NH}_2 + \text{HCl}$; (2) by the action of H_2SO_4 upon the unsaturated amins. Thus vinylamin yields oxyethylamin: $\text{CH}_2:\text{CH.NH}_2 + \text{H}_2\text{O} = \text{CH}_2\text{OH.CH}_2\text{NH}_2$; (3) Primary, secondary and tertiary oxyamins are formed by the union of ammonia with alkylene oxids: $(\text{CH}_2)_2\text{O} + \text{NH}_3 = \text{CH}_2\text{OH.CH}_2\text{NH}_2$; or $2(\text{CH}_2)_2\text{O} + \text{NH}_3 = (\text{CH}_2\text{OH.CH}_2)_2\text{NH}$; or $3(\text{CH}_2)_2\text{O} + \text{NH}_3 = (\text{CH}_2\text{OH.CH}_2)_3\text{N}$.

Cholin—*Trimethyloxethylammonium hydroxid*—*Bilineurin*—*Sin-calín*— $\begin{array}{c} \text{CH}_2\text{OH} \quad \text{OH} \\ | \quad \diagup \\ \text{CH}_2\text{.N}\equiv(\text{CH}_3)_3 \end{array}$ —occurs in hops, in fungi, in certain seeds, in the human placenta, in bile, in the yolks of eggs, and in the cerebrospinal fluid in epilepsy and other organic diseases of the nervous system. It is a constituent of the lecithins (p. 367). It is formed synthetically (as its chlorid) by the union of ethylene chlorhydrin and trimethylamin:



It is produced during the first forty-eight hours of putrefaction of animal tissues, from the decomposition of the lecithins, and diminishes from the third day, when other ptomaines (neuridin, putrescin, cadaverin) increase in amount. When heated, it splits up into glycol and trimethylamin. Nitric acid converts it into muscarin.

It is a thick syrup, soluble in H_2O and in alcohol, and strongly alkaline in reaction. Even in dilute aqueous solution it prevents the coagulation of albumin and redissolves coagulated albumin and fibrin. It is a strong base; attracts CO_2 from the air; forms with HCl a salt, soluble in alcohol, which crystallizes in plates and needles, resembling those of cholesterin. Its chloroplatinate is purified with difficulty; its chloroaurate readily. It is poisonous only in large doses.

Amanitin—*Trimethyloxethylideneammonium hydroxid*—*Isocholin*— $\begin{array}{c} \text{CH}_3 \quad \text{OH} \\ | \quad \diagup \\ \text{CHOH.N}\equiv(\text{CH}_3)_3 \end{array}$ —is an isomere of cholin, existing along with muscarin (see below) in *Agaricus muscarius*. It is produced by methylation of aldehydeammonia: $\text{CH}_3\text{.CHOH.NH}_2$. By oxidation with HNO_3 it yields muscarin.

Muscarin— $\begin{array}{c} \text{CH}_2\text{OH} \quad \text{OH} \\ | \quad \diagup \\ \text{CHOH.N}\equiv(\text{CH}_3)_3 \end{array}$ —is related to cholin, neurin and amanitin, from which it may be obtained by oxidation.

It occurs in nature in *Agaricus muscarius*, and is produced during putrefactive decomposition of proteins.

The free base occurs in very deliquescent, irregular crystals, or, if not perfectly dry, a colorless, odorless, and tasteless, but strongly alkaline syrup; readily soluble in all proportions in water and in alcohol; very sparingly soluble in chloroform; insoluble in ether. It is a more powerful base than ammonium hydroxid. When decomposed it yields trimethylamin. Its chloroplatinate crystallizes in octahedra. Its chlorid forms colorless, brilliant, deliquescent needles.

When administered to animals, muscarin causes increased secretion of saliva and tears; vomiting; evacuation of faeces, at first solid, later liquid; contraction of the pupils, almost to the extent of closure; diminution of the rapidity of the pulse; interference with respiration and locomotion; gradual sinking of the heart's action and

respiration; and death. Atropin prevents the action of muscarin and diminishes its intensity when already established.

Neurin—*Trimethylvinylammonium hydroxid*— $\begin{array}{c} \text{CH}_2 \quad \text{OH} \\ \parallel \quad \diagup \\ \text{CH} \cdot \text{N} \equiv (\text{CH}_3)_3 \end{array}$ —is a base resembling cholin, for which reason it is considered here, although its proper place is as a derivative of vinylamin (q. v.). It has been obtained from brain tissue and from the suprarenal capsule, probably as a product of decomposition of protagon. It is produced from cholin by boiling with baryta water. The same body is one of the alkaloids produced by the putrefaction of muscular tissue, and is endowed with poisonous qualities, resembling, but less intense than, those of muscarin.

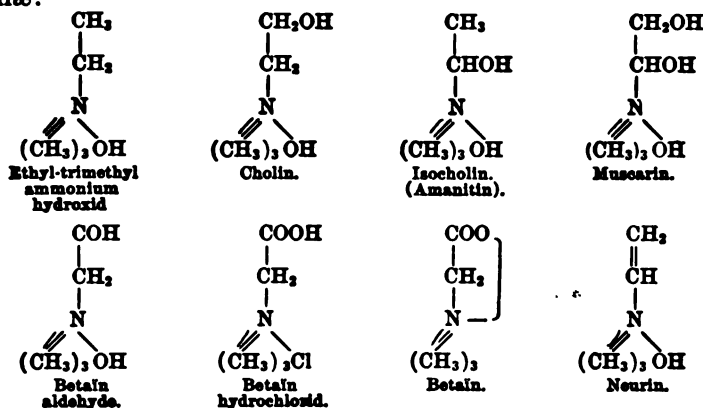
Betains—are lactams (p. 412) of hypothetical substances, such as that which would be derived from cholin: $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2 \cdot \text{N} \equiv (\text{CH}_3)_3 \end{array}$ by oxidation of the methoxyl group to a carboxyl: $\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{N} \equiv (\text{CH}_3)_3 \end{array}$. Although this substance, containing both carboxyl and basic hydroxyl, is unknown, the corresponding betain aldehyde and chlorid are known (see formulæ below).

The betains have the general formula: $\begin{array}{c} \text{COOH} \quad \text{OH} \\ | \quad \diagup \\ \text{R}'' - \text{N} \equiv \end{array}$, in which R'' may be any bivalent hydrocarbon radical, and in which the three remaining nitrogen valences may be satisfied by univalent radicals or by a trivalent radical. Or the arrangement of the valences may be reversed, as in nicotic-methyl betain: $\begin{array}{c} \text{COO} - \\ | \\ (\text{C}_5\text{H}_4)''' \equiv \text{N} - \text{CH}_3 \end{array}$.

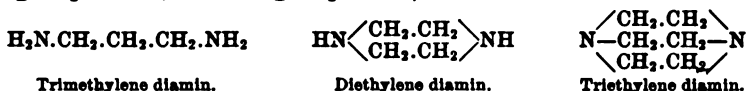
Betain—*Trimethyl-acetic betain*—*Oxyneurin*—*Oxycholin*—*Lycin*—*Trimethyl-glycocoll*— $\begin{array}{c} \text{COO} \\ | \\ \text{CH}_2 - \text{N} \equiv (\text{CH}_3)_3 \end{array}$ —was first obtained from beet-juice (*Beta vulgaris*). It exists in beet-sugar molasses, in cotton-seed, and in malt. It is formed by several synthetic methods, e. g., by the action of methyl iodid upon amido-acetic acid (p. 413): $\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2 \cdot \text{NH}_2 \end{array} + 3\text{CH}_3\text{I} = 3\text{HI} + \begin{array}{c} \text{COO} \\ | \\ \text{CH}_2 - \text{N} \equiv (\text{CH}_3)_3 \end{array}$; or by the interaction of monochloroacetic acid and trimethylamin: $\begin{array}{c} \text{COOH} \\ | \\ \text{CH}_2\text{Cl} \end{array} + \text{N}(\text{CH}_3)_3 = \begin{array}{c} \text{COO} \\ | \\ \text{CH}_2 - \text{N} \equiv (\text{CH}_3)_3 \end{array} + \text{HCl}$.

Betain crystallizes in large, deliquescent crystals, with one molecule of water of crystallization, very soluble in water and in alcohol. It is decomposed by heat with evolution of trimethylamin, a fact which is utilized to obtain that substance from beet-molasses. It is strongly basic and forms crystalline salts. Its chloraurate is crystalline and very sparingly soluble in cold water.

The relations of the oxyamin bases are shown in the following formulæ:



Diamins—are primary, secondary, and tertiary, as they contain two groups NH_2 , or two groups NH , or two N atoms:



The primary diamins only are acyclic compounds. They have the algebraic formula: $\text{N}_2\text{C}_n\text{H}_{2n+4}$; the secondary, $\text{N}_2\text{C}_n\text{H}_{2n+2}$; and the tertiary, $\text{N}_2\text{C}_n\text{H}_{2n}$. The secondary and tertiary diamins are not known beyond the ethylene compounds and are cyclic compounds (see Piperazin).

The primary diamins are obtained (1) by the reduction of the olefin dicyanids. Thus ethylene cyanid yields tetramethylene diamin: $\text{CN}.\text{CH}_2.\text{CH}_2.\text{CN} + 4\text{H}_2 = \text{H}_2\text{N}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$; (2) as hydrobromids, by heating the olefin bromids with alcoholic ammonia to 100° under pressure: $\text{BrCH}_2.\text{CH}_2\text{Br} + 2\text{NH}_3 = \text{H}_3\text{Br} :: \text{N}.\text{CH}_2.\text{CH}_2.\text{N} :: \text{H}_3\text{Br}$; (3) by reduction of the dinitroparaffins: $\text{NO}_2\text{CH}_2.\text{CH}_2\text{NO}_2 + 6\text{H}_2 = \text{H}_2\text{N}.\text{CH}_2.\text{CH}_2.\text{NH}_2 + 4\text{H}_2\text{O}$.

The diamins form crystalline, insoluble benzoyl derivatives when shaken in alkaline solution with benzoyl chlorid, a property which they share with polyatomic alcohols and hexoses.

Among the diamins are included several of the products of putrefaction known as ptomaines.

Ethylenediamin— $\text{H}_2\text{N}.\text{(CH}_2)_2.\text{NH}_2$ —is a strongly alkaline liquid, boiling at 116.5° (241.7°F.). With acetyl chlorid it forms diacetyl-ethylene diamin, $\begin{array}{c} \text{CH}_3.\text{NH}.\text{CO}.\text{CH}_3 \\ | \\ \text{CH}_2.\text{NH}.\text{CO}.\text{CH}_3 \end{array}$, which is decomposed by heat with formation of a cyclic amidin base (p. 388), ethylene-ethenyl amidin, or lysidin, $\begin{array}{c} \text{CH}_2.\text{NH} \\ | \\ \text{CH}_2.\text{N} \end{array} \text{C}.\text{CH}_3$ (p. 514).

Trimethylenediamin— $\text{H}_2\text{N} \cdot (\text{CH}_2)_3 \cdot \text{NH}_2$ —is said to have been obtained from the cultures of the comma bacillus. It has been obtained synthetically by the second method given on p. 385. It is an alkaline liquid, boiling at 135° (275°F.).

Tetramethylenediamin—Putrescin— $\text{H}_2\text{N} \cdot (\text{CH}_2)_4 \cdot \text{NH}_2$ —is produced, along with the cadaverin, during the putrefaction of muscular tissue, internal organs of man and animals, and of fish, and in the culture media of the comma bacillus from three days to four months. The free base is a colorless liquid (solid below 27°) having a seminal odor, which absorbs CO_2 from the air and unites with acids to form crystalline salts. It is not actively poisonous.

Pentamethylenediamin—Cadaverin— $\text{H}_2\text{N} \cdot (\text{CH}_2)_5 \cdot \text{NH}_2$ —is isomeric with neuridin and is produced during the later stages of putrefaction of many animal tissues, the cholin disappearing as this and the other diamins are formed. The free base is a clear syrupy liquid, having a strong disagreeable odor, resembling that of coniin, boils at 175° , and fumes in air. It absorbs CO_2 rapidly, with formation of a crystalline carbonate. Its salts are crystalline. The chlorid on dry distillation is decomposed into ammonium chlorid and piperidin (p. 519).

Hexamethylenediamin— $\text{H}_2\text{N} \cdot (\text{CH}_2)_6 \cdot \text{NH}_2$ —is formed during putrefaction of muscular tissue and pancreas. It is a crystalline solid, fusing at 40° (104°F.) and boiling at 195° (383°F.).

Neuridin— $\text{C}_5\text{H}_{14}\text{N}_2$ —a diamin of undetermined constitution, isomeric with cadaverin, is produced, along with cholin (p. 383), during the earlier stages of putrefaction, particularly of gelatinoid substances, and increases in quantity as putrefaction advances, while the quantity of cholin diminishes. The free base is a gelatinous substance, having a very marked seminal odor, readily soluble in water, insoluble in alcohol and in ether. Its chlorid is crystalline and very soluble in water. It seems to be non-poisonous when pure.

Saprin— $\text{C}_4\text{H}_{16}\text{N}_2$ —another diamin of undetermined constitution, has been obtained from putrid spleens and livers after three weeks' putrefaction.

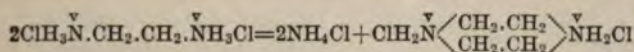
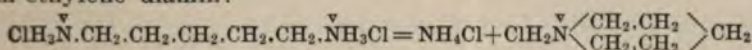
Mydalein is still another putrid product of undetermined composition, but probably a diamin containing four or five carbon atoms, which forms a difficultly crystallizable, hygroscopic chlorid, which is actively poisonous. Five milligrams administered hypodermically to a cat causes death after profuse diarrhoea and secretion of saliva, violent convulsions, and paralysis, beginning with the extremities and extending to the muscles of respiration.

Other diamins, in which alkyls are substituted for the remaining H of NH_2 , are formed by condensation of secondary amins with formic

aldehyde: $2(\text{CH}_3)_2\text{NH} + \text{H}.\text{CHO} = (\text{CH}_3)_2\text{N}.\text{CH}_2.\text{N}:(\text{CH}_3)_2 + \text{H}_2\text{O}$ and in them the alkyls may be like or unlike. And still other **diamidoparaffins**, or **diamins** in which one amido group is attached to a terminal carbon atom, and the other to an intermediate one, are known; such as 1, 4 diamido pentane: $\text{CH}_3.\text{CH}(\text{NH}_2).\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2$.

The **imins**, also called **imids** (but see p. 408), are formed by the substitution of bivalent hydrocarbon groups for two hydrogen atoms in a single molecule of ammonia; or they may be considered as derived from the dihydric alcohols by substitution of the imin group, $(\text{NH})''$ for both hydroxyls; the **diimins**, also called **diamids**, by the substitution of two such groups for four hydrogen atoms in two molecules of ammonia. These compounds are cyclic, and include some important members of the aromatic series.

When the diammonium chlorids are heated ammonium chlorid is split off, and an imin or a diimin is formed. Thus **piperidin** (p. 519) is produced from pentamethylene diamin; and **piperazin** (p. 522) from ethylene diamin:



Spermin— $\text{C}_2\text{H}_5\text{N}$ —probably **ethylene-imin**, $\overset{\text{CH}_2}{\underset{\text{CH}_2}{\text{N}}}\text{NH}$, has been obtained from semen, testicles, ovaries, prostate, thyroid, pancreas, and spleen. Its phosphate forms crystals, known as **Leyden**, **Böttcher's**, or **Charcot's** crystals, which are met with in anatomical preparations preserved in alcohol, in dried semen, in sputa and nasal secretions, in the blood, spleen, and other organs of leucocythæmics and anæmics, and in fæces. A substance, probably identical with spermin, is also found in the cultures of the comma bacillus on beef-broth. The free base forms crystals, which rapidly absorb carbon dioxid from air, are readily soluble in water and in alcohol, insoluble in ether, and strongly alkaline in reaction. The Charcot crystals are insoluble in alcohol, ether and chloroform, difficultly soluble in water, easily soluble in dilute acids or alkalies.

Glucosamins.—As the primary monamins, the hydramins and the diamins may be considered as derived from the monohydric and dihydric alcohols by substitution of NH_2 for OH (p. 378), so similar compounds may be derived from the aldoses and ketoses (p. 309).

Chitosamin, probably **d-glucosamin**, $\text{CH}_2\text{OH}.\text{(CHOH)}_3.\text{CHNH}_2.\text{-CHO}$, was first extracted from chitin (p. 597), and from certain fungi. It has also been obtained from urine, and exists in protein combination, probably in an amidopolysaccharid form (p. 309), and in glycoproteids (p. 594). It forms small, colorless crystals, f. p. 110° ,

permanent when dry, but decomposing in solution, dextrogyrous $[a]_D = +44^\circ$. It forms crystalline salts with acids, is not fermentable, and is converted by HNO_2 into a nonfermentable hexose, $\text{C}_6\text{H}_{12}\text{O}_6$, called **chitose**. It reduces the salts of Ag, Cu and Bi to the same extent as does glucose. **Isoglucosamin**, $\text{CH}_2\text{NH}_2\text{CO}(\text{CHOH})_3\text{CH}_2\text{OH}$, is obtained, as a lævogyrous, uncrystallizable, reducing syrup, by reduction of glucososazone (p. 485). **Acrosamin** is a reducing, optically inactive glucosamin, obtained by the reduction of acrososazone.

AMIDINS—AMIDOXIMS—HYDROXAMIC ACIDS.

The **amidins** contain both the amido group, NH_2 , and the imido group, NH , and have the general formula: $\text{R}.\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix}$, in which R is any univalent hydrocarbon radical.

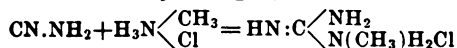
They are formed by heating the nitrils (p. 393) with ammonium chlorid. Thus acetonitril yields **acetamidin**: $\text{CH}_3.\text{C}:\text{N} + \text{NH}_4\text{Cl} = \text{HCl} + \text{CH}_3.\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix}$. They are also formed by action of HCl upon the amids. Indeed, they may be considered as being derived from the amids (p. 399) by substitution of NH for the carbonyl oxygen: $\text{CH}_3.\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{O} \end{smallmatrix}$, acetamid: $\text{CH}_3.\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix}$, acetamidin. The amidins are monacid bases, very unstable when free.

The **amidoxims** are derived from the amidins by substitution of OH for hydrogen, e. g., $\text{CH}_3.\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{N.OH} \end{smallmatrix}$, **ethenylamidoxim**. They are very unstable compounds, formed by the action of hydroxylamin upon nitrils or upon amidins (p. 409).

Hydroxamic acids contain the oxim group, N.OH , while the amido group of the amidin is replaced by hydroxyl: $\text{CH}_3.\text{C} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{N.OH} \end{smallmatrix}$, **aceto-hydroxamic acid**.

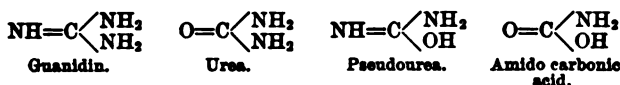
GUANIDIN AND ITS DERIVATIVES.

Guanidin—Carbotriamin— CH_5N_3 —was first obtained by oxidation of guanin (p. 534). It is formed (1) by heating ethyl orthocarbonate with ammonia: $\text{C}(\text{OC}_2\text{H}_5)_4 + 3\text{NH}_3 = \text{HN}:\text{C}:(\text{NH}_2)_2 + 4\text{CH}_3.\text{CH}_2\text{OH}$; (2) from cyanogen iodid and ammonia: $\text{CNI} + 2\text{NH}_3 = \text{HN}:\text{C}:(\text{NH}_2)_2 + \text{HI}$; (3) as hydrochlorid from cyanamid and ammonium chlorid: $\text{CN.NH}_2 + \text{NH}_4\text{Cl} = \text{ClH}_2:\text{N}:\text{C}:(\text{NH}_2)_2$. Substituted guanidins may be obtained by method (3) by using hydrochlorids of primary amins:



Guanidin, containing the group $\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix}$, is an amidin. It may also

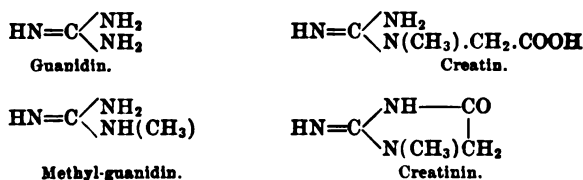
be considered as a triamin, derived from three ammonia molecules, $\text{H}_2\text{N}-\text{C}\begin{smallmatrix} \text{NH}_2 \\ \text{NH} \end{smallmatrix}$. It is related to amidocarbonic acid, to urea and to pseudourea, as is indicated by the formulæ:



It is a crystalline solid, which absorbs CO_2 and H_2O from the air, and forms crystalline salts. It is one of the sources from which hydrazin and its hydroxid and sulfate are most conveniently obtained. It is first converted into nitroguanidin, $\text{HN}:\text{C}\begin{smallmatrix} \text{NH}(\text{NO}_2) \\ \text{NH}_2 \end{smallmatrix}$. This is then reduced in presence of H_2SO_4 to amidoguanidin sulfate, $\text{HN}:\text{C}\begin{smallmatrix} \text{NH}(\text{NH}_2) \\ \text{N} \end{smallmatrix} \begin{smallmatrix} \text{H}_3 \\ \text{—HSO}_4 \end{smallmatrix}$, which is then hydrolyzed with formation of ammonia, carbon dioxid and hydrazin sulfate: $\text{H}_2\text{N}.\text{N}\begin{smallmatrix} \text{H}_3 \\ \text{—HSO}_4 \end{smallmatrix}$.

Methyl-guanidin — Methyluramin— $\text{HN}:\text{C}(\text{NH}_2)\text{NH}(\text{CH}_3)$ —was first obtained by the oxidation of creatin and of creatinin (see below). It has also been obtained as a product of putrefaction of muscular tissue at a low temperature in closed vessels, when it probably results from the decomposition of creatin. It is a colorless, crystalline, deliquescent, strongly alkaline substance, and is highly poisonous.

The relation of guanidin and methyl-guanidin to each other and to creatin and creatinin is shown by the following formulæ:



Creatin—Methyl-guanidin acetic acid— $\text{C}_4\text{H}_9\text{N}_3\text{O}_2 + \text{Aq}$ —is, as is shown by the above graphic formula, a complex amido-acid (p. 411). It is a normal constituent of the juices of muscular tissue, brain, blood, and amniotic fluid. It is formed synthetically by the union of methyl glycooll (p. 414), and cyanamid (p. 398): $\text{CH}_2(\text{NH}.\text{CH}_3).\text{COOH} + \text{NC}.\text{NH}_2 = \text{HN}=\text{C}\begin{smallmatrix} \text{NH}_2 \\ \text{N}(\text{CH}_3) \end{smallmatrix}.\text{CH}_2.\text{COOH}$.

It is best obtained from the flesh of the fowl, which contains 0.32 per cent., or from beef-heart, which contains 0.14 per cent. It is soluble in boiling H_2O and in alcohol, insoluble in ether; crystallizes in brilliant, oblique, rhombic prisms; neutral; tasteless; loses Aq at 100° (212°F.); fuses and decomposes at higher temperatures. When long heated with H_2O , or treated with concentrated acids, it loses H_2O , and is converted into creatinin. Baryta water decomposes it

into sarcosin and urea. It is not precipitated by silver nitrate, except when it is in excess and in presence of a small quantity of potassium hydroxid. The white precipitate so obtained is soluble in excess of potash, from which a jelly separates, which turns black, slowly at ordinary temperatures, rapidly at 100° (212° F.). A white precipitate, which turns black when heated, is also formed when a solution of creatin is similarly treated with mercuric chlorid and potash.

Creatinin—*Methyl-guanidin acetic lactam*— $C_4H_7N_3O$ —113—a product of the dehydration of creatin, is a normal and constant constituent of the urine and amniotic fluid, and also exists in the blood and muscular tissue.

It crystallizes in oblique, rhombic prisms, soluble in H_2O and in hot alcohol, insoluble in ether. It is a strong base, has an alkaline taste and reaction; expels NH_3 from the ammoniacal salts, and forms well-defined salts, among which is the double chlorid of zinc and creatinin ($C_4H_7N_3O$) $_2ZnCl_2$, obtained in very sparingly soluble, oblique prismatic crystals, when alcoholic solutions of creatinin and zinc chlorid are mixed.

Cruso-creatinin— $C_5H_8N_4O$ —is an orange-yellow, crystalline solid, alkaline in reaction; **Xantho-creatinin**— $C_5H_{10}N_4O$ —is in yellow crystalline plates; **Amphi-creatinin**— $C_9H_{10}N_7O_4$ —forms yellowish-white prismatic crystals. These are basic substances, forming crystalline chlorids, and belonging to the class of **leucomains**, which include basic nitrogen compounds produced by physiological processes. (See p. 571.) They are obtained from the juices of muscular tissue, and from Liebig's meat extract, in which they accompany creatin and creatinin.

HYDRAZINS—HYDRAZIDS.

The **hydrazins** are derivatives of hydrazin or diamidogen, $H_2N.NH_2$ (p. 152), by substitution of aliphatic or aromatic radicals, alcoholic, phenolic or acid, for one or more of the hydrogen atoms in the same way as the amins are derived from ammonia. There are, therefore, primary, secondary, tertiary and quaternary hydrazins; and they may be **symmetrical**, as $C_2H_5.HN.NH.C_2H_5$ and $C_6H_5.HN.NH.C_2H_5$, or **unsymmetrical**, as $C_6H_5.HN.NH_2$ and $(C_2H_5)_2N.NH_2$. The aliphatic hydrazins are obtained from the alkyl-ureas, by conversion into nitroso-amins, and reduction. Most of the hydrazins, some of which are of considerable interest, are derivatives of phenyl-hydrazin, $C_6H_5.HN.NH_2$, and, containing a cyclic chain C_6H_5 . These will be considered among the aromatic compounds. The **hydrazids**, corresponding to the amids, contain acidyls.

NITRILS—CYANOGEN COMPOUNDS.

These substances may be considered either as compounds of the univalent radical **cyanogen** $(\text{CN})'$, or as paraffins, $\text{C}_n\text{H}_{2n+2}$, in which three atoms of hydrogen have been replaced by the trivalent N''' atom, hence **nitrils**, compounds of N with the trivalent radicals $\text{C}_n\text{H}_{2n-1}$.

Hydrogen Cyanid—*Formonitril*—*Cyanogen hydrid*—**Hydrocyanic acid**—**Prussic acid**— $\text{HC}\text{:}\text{N}$ —exists ready formed in the juice of *cassava*, and is formed by the action of H_2O upon bitter almonds, cherry-laurel leaves, and other vegetable products containing **amygdalin**, a glucosid, which is decomposed into glucose, benzoic aldehyde (p. 466), and hydrocyanic acid, when warmed with water. It is also formed in a great number of reactions: by the passage of the electric discharge through a mixture of acetylene and nitrogen: $\text{HC}\text{:}\text{CH} + \text{N}_2 = 2\text{HC}\text{:}\text{N}$; by the action of chloroform on ammonia: $\text{NH}_3 + \text{CHCl}_3 = 3\text{HCl} + \text{HCN}$; by the distillation of, or the action of HNO_3 upon, many organic substances; by the decomposition of cyanids (see Nitrils, below).

It is always prepared by the decomposition of a cyanid or a ferrocyanid, usually by acting upon potassium ferrocyanid with dilute sulfuric acid, and distilling. Its preparation in the pure form is an operation attended with the most serious danger, and should only be attempted by those well trained in chemical manipulation. For medical uses a very dilute acid is required; the **acid. hydrocyanicum dil.** (U. S. Br.) contains, if freshly and properly prepared, two per cent. of anhydrous acid. That of the French Codex is much stronger—ten per cent.

The pure acid is a colorless, mobile liquid, has a penetrating and characteristic odor; sp. gr. 0.7058 at 7° (44.6° F.); crystallizes at -15° (5° F.); boils at 26.5° (79.7° F.); is rapidly decomposed by exposure to light. The dilute acid of the U. S. P. is a colorless liquid, having the odor of the acid; faintly acid, the reddened litmus returning to blue on exposure to air; sp. gr. 0.997; 10 grams of the acid should react without excess with 1.27 gram of silver nitrate. The dilute acid deteriorates on exposure to light, although more slowly than the concentrated; a trace of phosphoric acid added to the solution retards the decomposition.

Most strong acids decompose HCN . The alkalis enter into double decomposition with it to form **cyanids**. It is decomposed by Cl and Br, with formation of cyanogen chlorid or bromid. Nascent H converts it into methylamin. With aldehydes and ketones it forms cyanhydrins as additive products (p. 397). The pure acid or its concentrated solutions readily polymerize on contact with KCN to form colored polymeres and one which is crystalline and colorless. (See **Amido-malononitril**, p. 395.)

Analytical Characters.—(1) With silver nitrate: a dense, white ppt.; which is not dissolved on addition of HNO_3 to the liquid, but dissolves when separated and heated with concentrated HNO_3 ; soluble in solutions of alkaline cyanids or thiosulfates. (2) Treated with NH_4HS , evaporated to dryness, and ferric chlorid added to the residue: a blood-red color, which is discharged by mercuric chlorid. (3) With potash and then a mixture of ferrous and ferric sulfates: a greenish ppt., which is partly dissolved by HCl , leaving a pure dark-blue precipitate. (4) Heated with a dilute solution of picric acid and then cooled: a deep-red color. (5) Moisten a piece of filter-paper with a freshly prepared alcoholic solution of guaiac; dip the paper into a very dilute solution of CuSO_4 , and, after drying, into the liquid to be tested. In the presence of HCN it assumes a deep-blue color. (6) Add a few drops of potassium nitrite solution, then two or three drops of ferric chlorid solution, and enough dilute H_2SO_4 to turn the color to yellow. Heat just to boiling; cool, add a few drops of NH_4HO , filter, and add to the filtrate a few drops of dilute, colorless ammonium sulfhydrate: a violet color, changing to blue, then to green and yellow (p. 399).

Toxicology.—Hydrocyanic acid is a violent poison, whether it be inhaled as vapor, or swallowed, either in the form of dilute acid, of soluble cyanid, or of the pharmaceutical preparations containing it, such as oil of bitter almonds and cherry-laurel water; its action being more rapid when taken by inhalation or in aqueous solution than in other forms. When the medicinal acid is taken in poisonous dose, its lethal effect may seem to be produced instantaneously; nevertheless, several respiratory efforts usually are made after the victim seems to be dead, and instances are not wanting in which there was time for considerable voluntary motion between the time of ingestion of the poison and unconsciousness. In the great majority of cases the patient is either dead or fully under the influence of the poison on the arrival of the physician, who should, however, not neglect to apply the proper remedies if the faintest spark of life remain. Chemical antidotes are, owing to the rapidity of action of the poison, of no avail, although possibly chlorin, recommended as an antidote by many, may have a chemical action on that portion of the acid already absorbed. The treatment indicated is directed to the maintenance of respiration; cold douche, galvanism, artificial respiration, until elimination has removed the poison. If the patient survive an hour after taking the poison, the prognosis becomes very favorable; in the first stages it is exceedingly unfavorable, unless the quantity taken has been very small.

In cases of death from hydrocyanic acid the odor of the poison may be observed in the apartment, or upon opening the body. In

cases of suicide or accident, the vessel from which the poison has been taken will usually be found near the body, although the absence of such vessel is not proof that the case is one of homicide.

Notwithstanding the volatility and instability of the poison, its presence has been detected two months after death, although the chances of separating it are certainly the better the sooner after death the analysis is made. The search for hydrocyanic acid is combined with that of phosphorus; the part of the distillate containing the more volatile products is examined by the tests given above. It is best, when the presence of free hydrocyanic acid is suspected, to distil at first without acidulating. In cases of suspected homicide by hydrocyanic acid, the stomach should never be opened until immediately before the analysis.

Cyanogen Chlorids.—Two polymeric chlorids are known: **Cyanogen chlorid**, CNCl , formed by the action of Cl upon anhydrous HCN or upon $\text{Hg}(\text{CN})_2$ in the dark. It is a colorless gas, condensing to a liquid at 15° (59°F.); intensely irritating and poisonous. **Tricyanogen chlorid**, $\text{C}_3\text{N}_3\text{Cl}_3$, is formed, as a crystalline solid, when anhydrous HCN is acted upon by Cl in sunlight. It fuses at 146° . (See Cyanidin, p. 537.)

Cyanids.—The most important of the simple metallic cyanids are those of K and Ag (pp. 228, 231, also p. 398).

Nitrils.—The **hydrocyanic esters** of the univalent alcoholic radicals are called **acid nitrils**, because of their formation from the amids (p. 400), by the reaction given under (3) below. Hydrocyanic acid, being produced from formamid, is **formonitril**; methyl cyanid, derived from acetamid, is **acetonitril**, etc. They are also derivable from the ammonium salt of the acid by elimination of the elements of two molecules of water. Their formulæ may be derived from those of the acids by substitution of N for the trivalent OOH of the carboxyl. They are not to be confounded with the acidyl cyanids, which are the nitrils of the ketonic acids (p. 398).

The nitrils are produced: (1) By heating the haloid esters (p. 277) with alcoholic solution of potassium cyanid at 100° : $\text{CH}_3.\text{CH}_2\text{I} + \text{KCN} = \text{CH}_3.\text{CH}_2.\text{CN} + \text{KI}$. (2) By distilling a mixture of potassium cyanid and the potassium salt of a monoalkyl sulfate. Thus, ethyl cyanid is produced from potassium ethylsulfate: $\text{KCN} + \text{SO}_4.\text{C}_2\text{H}_5.\text{K} = \text{K}_2\text{SO}_4 + \text{C}_2\text{H}_5.\text{CN}$. (3) By complete dehydration, by the action of P_2O_5 , of the ammoniacal salt of the acid, or of its amid (p. 400). Thus acetonitril is obtained from ammonium acetate: $\text{CH}_3.\text{COO}(\text{NH}_4) = \text{CH}_3.\text{CN} + 2\text{H}_2\text{O}$; or from acetamid: $\text{CH}_3.\text{CO}.\text{NH}_2 = \text{CH}_3.\text{CN} + \text{H}_2\text{O}$. (4) By the action of acidyl chlorids upon silver cyanate. Thus, with acetyl chlorid, methyl cyanid is formed: $\text{CNO}.\text{Ag} + \text{CH}_3.\text{CO}.\text{Cl} = \text{AgCl} + \text{CO}_2 + \text{CH}_3.\text{CN}$.

The nitrils combine with nascent hydrogen to form primary amines. Thus acetonitril forms ethylamin: $\text{CH}_3.\text{CN} + 2\text{H}_2 = \text{C}_2\text{H}_5.\text{NH}_2$. Hydrating agents convert them into the ammonium salts of the corresponding acids. Thus ammonium propionate is derived from ethyl cyanid: $\text{C}_2\text{H}_5.\text{CN} + 2\text{H}_2\text{O} = \text{C}_2\text{H}_5.\text{COO}(\text{NH}_4)$. Or, when acted upon by concentrated sulfuric acid, hydrogen peroxid, or concentrated hydrochloric acid, they take up one molecule of water and form amids (p. 400). Thus acetonitril forms acetamid: $\text{CH}_3.\text{CN} + \text{H}_2\text{O} = \text{CH}_3.\text{CO}.\text{NH}_2$. The nitrils above acetonitril readily polymerize to form alkyl paratriazines (p. 537).

Methyl Cyanid—Acetonitril— $\text{CH}_3.\text{CN}$ —is a colorless liquid, b. p. 81.6° , having an agreeable odor, sparingly soluble in water, obtained by distilling ammonium acetate or acetamid with P_2O_5 .

The **isocyanids**, **carbylamins**, or **carbamins** are isomeres of the nitrils, which differ from the latter in constitution in that, in the nitrils, the nitrogen is trivalent, and the alkyl group is in union with carbon, e. g., methyl cyanid, $\text{N}\equiv\text{C}-\text{CH}_3$, while in the carbylamins the nitrogen is quinivalent, and the alkyl is in union with nitrogen, e. g., methyl isocyanid, $\text{C}\equiv\text{N}-\text{CH}_3$. The difference in constitution between the nitrils (alkyl cyanids) and the alkyl isocyanids is shown by the difference in their behavior with hydrating agents. While the cyanids yield the ammonium salts of the corresponding acids: $\text{CH}_3.\text{CH}_2.\text{CN} + 2\text{H}_2\text{O} = \text{CH}_3.\text{CH}_2.\text{COO}(\text{NH}_4)$, the isocyanids are split into a primary amin and formic acid: $\text{CH}_3.\text{CH}_2.\text{NC} + 2\text{H}_2\text{O} = \text{CH}_3.\text{CH}_2.\text{NH}_2 + \text{H}.\text{COOH}$.

The isocyanids are formed: (1) by the action of a primary monamin on chloroform in the presence of caustic potash. Thus methyl isocyanid is derived from methylamin: $\text{CH}_3.\text{NH}_2 + \text{CHCl}_3 = 3\text{HCl} + \text{NC}.\text{CH}_3$. (pp. 279, 380); (2) by the action of alkyl iodids upon silver cyanid: $\text{CH}_3\text{I} + \text{AgCN} = \text{AgI} + \text{NC}.\text{CH}_3$.

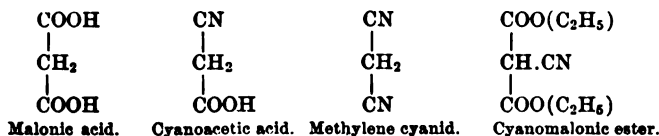
Methyl Isocyanid—Methyl carbylamin—Isoacetonitril— $\text{CH}_3.\text{NC}$ —is a colorless liquid, b. p., 58° , having a disagreeable odor, and giving off highly poisonous vapor. It is formed by the reactions given above, and is said to exist in the venom of toads.

Phenyl Isocyanid—Isobenzonitril— $\text{C}_6\text{H}_5.\text{NC}$ —is a colorless liquid, not boiling without decomposition, having an intensely disagreeable odor, whose formation is utilized in a test for chloroform (p. 279).

Both nitrils and isonitrils combine with the hydracids to form crystalline salts, decomposable by water; the latter much more energetically than the former. They are all volatile liquids; the nitrils having ethereal odors when pure, the isonitrils odors which are very powerful and disagreeable.

Nitrils of Dicarboxylic Acids.—Two nitrils are derivable from each acid of this series, one being an acid nitril, or **nitrilic acid**, the other a

dinitril, or dicyanid. The nitrilic acids are **cyano-fatty acids**, and the dinitrils, beyond the first, are the **alkylen dicyanids**. Corresponding to malonic acid there exists also a cyanomalonic ester, in which the CN is substituted in the CH_2 group. (See p. 361):



The nitrilic acid of oxalic acid is only known in its esters; its dinitril is dicyanogen, which differs from the alkylen dicyanids, which are its superior homologues, in containing no hydrocarbon group.

Cyano-fatty Acids—include not only the nitrilic acids, in which the CN is in a terminal group, but also compounds such as α cyano-propionic acid, $\text{CH}_2\text{CHCN.COOH}$.

The nitrilic acids are obtained from the monochloro-fatty acids: $\text{CH}_2\text{Cl.COOH} + \text{KCN} = \text{CH}_2\text{CN.COOH} + \text{KCl}$. When heated they are decomposed to nitrils and carbon dioxid: $\text{CH}_2\text{CN.COOH} = \text{CH}_3\text{.CN} + \text{CO}_2$. By acids and alkalies they are hydrated to dicarboxylic acids: $\text{CH}_2\text{CN.COOH} + 2\text{H}_2\text{O} = \text{COOH.CH}_2\text{.COOH} + \text{NH}_3$. With ammonia they produce amids (p. 400). Thus cyanacetamid is formed from cyanacetic acid: $\text{CH}_2\text{CN.COOH} + \text{NH}_3 = \text{CN.CH}_2\text{.CONH}_2 + \text{H}_2\text{O}$.

Dicyanogen— CN.CN —is prepared by heating mercuric cyanid, and is also formed by passing an electric arc between carbon points in an atmosphere of nitrogen.

It is a colorless gas, has a pronounced odor of bitter almonds: sp. gr., 1.8064 A. It burns in air with a purple flame, giving off N and CO_2 . It is quite soluble in water, but the solutions soon turn brown, and then contain ammonium oxalate and formate, urea, and hydrocyanic acid. The brown color is due to the formation of **azulmic acid**, $\text{C}_4\text{H}_5\text{N}_5\text{O}$.

The **alkylen dicyanids** are obtained: (1) from the alkylen bromids: $\text{CH}_2\text{Br.CH}_2\text{Br} + 2\text{KCN} = \text{CN.CH}_2\text{.CH}_2\text{.CN} + 2\text{KBr}$; (2) by dehydration of the amids of cyano-fatty acids: $\text{CN.CH}_2\text{.CO.NH}_2 = \text{CN.CH}_2\text{.CN} + \text{H}_2\text{O}$. By nascent hydrogen they are converted into diamins (p. 385); and by hydrolysis into dicarboxylic acids (p. 335).

Malononitril—*Methylene cyanid*— $\text{CN.CH}_2\text{.CN}$ —is obtained from cyanacetamid by (2) above. It would be isomeric with the unknown **cyaniform**, $\text{CH}(\text{CN})_3$. The crystalline polymere of hydrocyanic acid (p. 391) is presumed to be **amido-malononitril**, as it splits on hydrolysis to amidoacetic acid, carbon dioxid and ammonia: $\text{CN.CH}(\text{NH}_2).\text{CN} + 4\text{H}_2\text{O} = \text{CH}_2(\text{NH}_2).\text{COOH} + \text{CO}_2 + 2\text{NH}_3$.

Nitrils of Carbonic and Thiocarbonic Acids.—These constitute the oxygen and sulfur compounds of cyanogen. Thus cyanic acid

is the nitril of carbonic acid: $\text{CO}_2\text{H}(\text{NH}_4)^+ = \text{CONH} + 2\text{H}_2\text{O}$, and thiocyanic acid that of thiocarbonic acid: $\text{CO}_2\text{SH}(\text{NH}_4)^+ = \text{CSNH} + 2\text{H}_2\text{O}$.

Three structural formulæ of these compounds are possible: $\text{N}\equiv\text{C}.\text{OH}$, $\text{O}=\text{C}=\text{N.H}$, and $\text{C}\equiv\text{N.OH}$. The first structure is that of the normal cyanic and thiocyanic acids, the second that of the isocyanates and isothiocyanates, the third that of fulminic acid.

Cyanic Acid— NC.OH —is obtained by distillation of cyanuric acid, or, in its salts, by calcining the cyanids in presence of an oxidizing agent, or by the action of dicyanogen upon solutions of the alkalis or alkaline carbonates.

It is a colorless liquid, only stable below 0° (32°F.); has a strong odor, resembling that of formic acid; and is soluble in water; gives off an irritating vapor; is vesicating to the skin; and is changed by exposure to air into its polymere, **cyamelid**, a white, porcelain-like solid.

Cyanuric Acid—*Tricyanic acid*—*Trioxycyanidin* (p. 537)— $\text{HO}.\text{C}\begin{smallmatrix} \text{N}=\text{C}(\text{OH}) \\ \text{N}=\text{C}(\text{OH}) \end{smallmatrix}\text{N}$ —is produced by dry distillation of uric acid; by the action of heat or of Cl upon urea; by heating tricyanogen chlorid or bromid with water or with alkalis. It forms colorless crystals, odorless, almost tasteless, feebly acid, rather soluble in water. It is tribasic. It may be dissolved in strong H_2SO_4 or HNO_3 without decomposition, but, when boiled with acids or alkalis, it is decomposed into carbon dioxid and ammonia; and, when distilled, into cyanic acid.

The ordinary potassium and ammonium cyanates are regarded as **isocyanates**, salts of **isocyanic acid**, or **carbimid**, $\text{O}:\text{C}:\text{NH}$. The ammonium salt, $\text{O}:\text{C}:\text{N}(\text{NH}_4)^+$, is converted into its isomere, urea, $\text{H}_2\text{N.CO.NH}_2$, by evaporation of its solution. The isocyanic esters serve for the generation of the alkyl ureas (p. 406).

Fulminic Acid—*Carbyloxim*— $\text{C}\equiv\text{N.OH}$ —is a strongly acid substance, having the odor and poisonous qualities of hydrocyanic acid, whose Ag and Hg salts are formed by the action of nitrous acid upon alcohol and silver, or mercuric, nitrate. **Mercuric fulminate**, or **fulminating mercury**, crystallizes in white, soluble needles, and explodes violently upon shock. It is used in percussion caps, primers and cartridges. **Silver fulminate** is more violently explosive than the mercurial salt. **Fulminating gold** is not a fulminate, but **auro-amidoimid**, $\text{Au}(\text{NH})\text{NH}_2 + 3\text{H}_2\text{O}$.

Fulminuric Acid— $\text{CN.CH}(\text{NO}_2).\text{C}\begin{smallmatrix} \text{OH} \\ \text{NH} \end{smallmatrix}$ —metamerie with cyanuric, and polymeric with cyanic and isocyanic acids, is a derivative of tartronic acid, COOH.CHOH.COOH ; whose alkali salts are formed by boiling solutions of alkaline chlorids with mercuric fulminate.

Thiocyanic Acid—*Sulfocyanic acid*—*Cyanogen sulfhydrate*— $\text{N}\equiv$

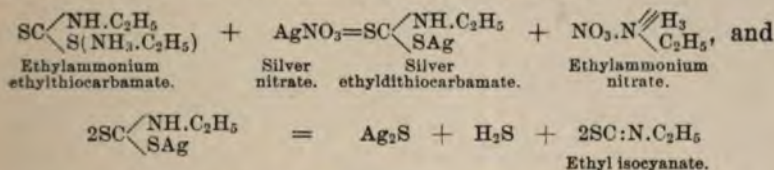
C.SH—is obtained by decomposition of its salts, which are formed by boiling solutions of the cyanids with sulfur; by the action of dicyanogen upon the metallic sulfids; and in several other ways.

The free acid is a colorless liquid, crystallizes at -12.5° (9.5° F.), acid in reaction. The prominent reaction of the acid and of its salts is the formation of a deep-red color with the ferric salts; the color being discharged by mercuric chlorid solution.

Thiocyanates exist in the human saliva and in the stomach-contents, in small amount. The free acid is poisonous.

Isothiocyanic Esters—Mustard oils—Isothiocyanic acid, S:C:NH , is not known in the free state. Its esters are called mustard oils, from the most important of the class, allyl isothiocyanate (p. 432), which is the essential oil of mustard.

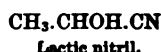
The mustard oils are obtained: (1) by mixing ether solutions of primary amines and carbon disulfid, and evaporating the solutions, the amin salts of alkyl dithiocarbamic acids are formed (p. 405): $\text{CS}_2 + 2\text{C}_2\text{H}_5\text{NH}_2 = \text{SC} \begin{smallmatrix} \text{NH.C}_2\text{H}_5 \\ \text{S(NH}_3\text{.C}_2\text{H}_5) \end{smallmatrix}$. On boiling aqueous solutions of these with AgNO_3 , Fe_2Cl_6 or HgCl_2 , the metallic sulfids are precipitated, and hydrogen sulfid and the mustard oils are formed, the latter distilling over. The reaction takes place in two stages:



Hoffmann's test for the primary amines (p. 380) is based upon these reactions.

The mustard oils are liquids, insoluble in water, giving off vapors of penetrating odor and irritating to the eyes. When heated with water under pressure to 200° (392° F.), or with hydrochloric acid to 100° (212° F.), they are decomposed into carbon dioxide, hydrogen sulfid and amines: $\text{SC:N.C}_2\text{H}_5 + 2\text{H}_2\text{O} = \text{CO}_2 + \text{SH}_2 + \text{NH}_2\text{.C}_2\text{H}_5$. Heating with dilute H_2SO_4 decomposes them into amines and carbon oxy-sulfid, COS. With nascent hydrogen they yield thioformaldehyde and a primary amine: $\text{SC:N.C}_2\text{H}_5 + 2\text{H}_2 = \text{H.CSH} + \text{NH}_2\text{.C}_2\text{H}_5$. Heated with monocarboxylic acids they form carbon oxysulfid, esters, and monamids (p. 399): $\text{SC:N.C}_2\text{H}_5 + 2\text{CH}_3\text{.COOH} = \text{COS} + \text{CH}_3\text{.COO.C}_2\text{H}_5 + \text{NH}_2\text{.CH}_3\text{.CO}$. Their alcoholic solutions, when boiled with HgO , yield isocyanic esters, which are converted by water into the corresponding compound ureas.

Nitrils of the Oxyacids.—The nitrils of the α -acids of the oxyacetic series (p. 339) are also called cyanhydrins, or oxycyanids, and bear the same relation to the acids as exists between the acids of the acetic series and their nitrils.



They are formed as additive products between hydrocyanic acid and the aldehydes and ketones: $\text{HCN} + \text{CH}_3.\text{CHO} = \text{CH}_3.\text{CHOH}.\text{CN}$, and $\text{HCN} + \text{CH}_3.\text{CO}.\text{CH}_3 = \text{CH}_3 > \text{C} \begin{smallmatrix} \text{CN} \\ \text{OH} \end{smallmatrix}$. By hydration they yield the corresponding acid and ammonia: $\text{CH}_3.\text{CHOH}.\text{CN} + 2\text{H}_2\text{O} = \text{CH}_3.\text{CHOH}.\text{COOH} + \text{NH}_3$. These reactions are utilized in the synthesis of the oxyacids (p. 339).

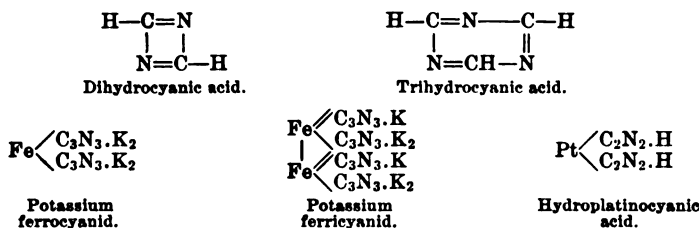
Nitrils of the Ketone Acids.—These are the cyanids of the acidyls, as the nitrils are the cyanids of the alkyls, and are formed by heating the acidyl chlorids with silver cyanid. Thus **acetyl cyanid** is produced from acetyl chlorid: $\text{CH}_3.\text{CO}.\text{Cl} + \text{AgCN} = \text{CH}_3.\text{CO}.\text{CN} + \text{AgCl}$; or by dehydration of the aldoxims (p. 409) of the α -aldehyde ketones. Thus oximido-acetone yields acetyl cyanid: $\text{CH}_3.\text{CO}.\text{CH}:\text{N}.\text{OH} = \text{CH}_3.\text{CO}.\text{CN} + \text{H}_2\text{O}$. They are unstable, and are decomposed by water into hydrocyanic acid and their corresponding acids: $\text{CH}_3.\text{CO}.\text{CN} + \text{H}_2\text{O} = \text{CH}_3.\text{COOH} + \text{CNH}$.

Cyanamid— $\text{CN}.\text{NH}_2$ —is the nitril of carbamic acid (p. 402): $\text{OC}:\text{NH}_2.\text{O}.\text{NH}_4.-2\text{H}_2\text{O} = \text{CN}.\text{NH}_2$. It is formed by the action of cyanogen chlorid upon ammonia: $\text{CNCl} + 2\text{NH}_3 = \text{NH}_4\text{Cl} + \text{CN}.\text{NH}_2$; or by the action of thionyl chlorid upon urea: $\text{NH}_2.\text{CO}.\text{NH}_2 + \text{SOCl}_2 = \text{CN}.\text{NH}_2 + \text{SO}_2 + 2\text{HCl}$. It forms colorless crystals, soluble in water, alcohol or ether. Corresponding to it are substituted cyanamids, which may be formed by using a primary amin in place of ammonia in the above-mentioned method of preparation: $\text{CNCl} + 2\text{NH}_2.\text{CH}_3 = \text{NH}_3.\text{CH}_3.\text{Cl} + \text{CN}.\text{NHCH}_3$. Heated with ammonium chlorid it forms guanidin hydrochlorid: $\text{CN}.\text{NH}_2 + \text{NH}_4\text{Cl} = \text{H}_3\text{CIN}.\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH}_2 \end{smallmatrix}$. Hydrating agents convert it into urea: $\text{CN}.\text{NH}_2 + \text{H}_2\text{O} = \text{H}_2\text{N}.\text{CO}.\text{NH}_2$.

Metallocyanids.—The metallic compounds of cyanogen, the cyanids, may be divided into three classes: (1) the simple cyanids, such as potassium, silver, or mercuric cyanid, which resemble in constitution and general characters the chlorids, bromids and iodids; (2) the double cyanids, such as $\text{AgK}(\text{CN})_2$, or $\text{HgK}_2(\text{CN})_4$, which are constituted like other double salts. These salts have crystalline forms and solubilities of their own, independent of those of the simple cyanids of which they are made up. They are readily decomposed by cold acids, with liberation of hydrocyanic acid; (3) compound cyanids, or metallocyanids, in which the cyanogen groups are more intimately attached to the metal, in such manner that the ordinary analytical characters of the metals are completely masked; and when they are decomposed by cold acids hydrocyanic acid is not liberated,

but a complex metallohydrocyanic acid, corresponding in constitution to the salt. The metals entering into the composition of the metalocyanids are iron (ferro- and ferricyanids), cobalt (cobalticyanids), and platinum (platinocyanids); also chromium and manganese in the *ic* form.

The metalocyanids are considered as derivatives of two hypothetical acids, polymeres of hydrocyanic acid: **dihydrocyanic acid** and **trihydrocyanic acid** (see Paratriazin, p. 537), which, in the hydrometallo-cyanic acids and their salts, are combined with the constituent metal, with loss of hydrogen, as shown in the following formulæ:



Hydronitroprussic Acid— $\text{Fe}(\text{CN})_5(\text{NO})\text{H}_2$ —contains the *nitroso* group NO, and is produced when potassium ferrocyanid is acted upon by nitric acid. Its sodium salt, **sodium nitroprussid**, is formed by neutralizing the acid with sodium carbonate. It forms brilliant red prisms; and is used as a test for sulfids, with which it forms a violet color. (See test No. 6, Hydrocyanic acid, p. 391.)

AMIDS.

These compounds are similar in constitution to the amins (p. 377,) from which they differ in that the radicals substituted in ammonia are acidyls in place of alkyls: $\text{N} \begin{array}{l} \diagup \text{CO} \cdot \text{CH}_3 \\ \diagdown \text{H}_2 \end{array}$; $\text{N} \begin{array}{l} \diagup (\text{CO} \cdot \text{CH}_3)_2 \\ \diagdown \text{H} \end{array}$; $\text{N}(\text{CO} \cdot \text{CH}_3)_3$.

Like the amins they are classified into **monamids**, **diamids**, **tri-amids**, according as they are derived from one, two or three molecules of ammonia.

Mixed amids are also known, produced by the substitution of acid radicals for the remaining hydrogen of the primary and secondary amins, e. g., diethyl acetamid: $\text{CH}_3\text{CO}(\text{C}_2\text{H}_5)_2\text{N}$.

MONAMIDS—AMIC ACIDS—IMIDS.

Like the monamins, the monamids are **primary**, **secondary**, or **tertiary**, as they contain one, two or three substituted radicals.

The primary monamids corresponding to the monocarboxylic acids may also be considered as being derived from those acids by substi-

tution of NH_2 for the OH of the group COOH ; as the amines are derivable from the alcohols by substitution of NH_2 for OH in CH_2OH , CHOH or COH . Thus acetamid, $\text{CH}_3\text{CO.NH}_2$ is derived from acetic acid, $\text{CH}_3\text{CO.OH}$.

The **primary monamids** are formed: (1) by the action of heat upon the ammonium salt of the acid, with elimination of the elements of one molecule of water: $\text{CH}_3\text{COO(NH}_4\text{)}=\text{H}_2\text{O}+\text{CH}_3\text{CO.NH}_2$. It will be remembered that the nitrils (p. 393) are derived from the ammoniacal salts by elimination of two molecules of water: $\text{CH}_3\text{COO(NH}_4\text{)}=2\text{H}_2\text{O}+\text{CH}_3\text{CN}$; (2) by addition of H_2O to the nitrils. Thus hydrogen peroxid in alkaline solution converts acetonitril into acetamid: $2\text{CH}_3\text{CN}+2\text{H}_2\text{O}_2=2\text{CH}_3\text{CO.NH}_2+\text{O}_2$; (3) by the action of ammonia upon esters. Thus, ethyl acetate and ammonia produce acetamid and ethylic alcohol: $\text{CH}_3\text{COO(C}_2\text{H}_5\text{)}+\text{NH}_3=\text{CH}_3\text{CO.NH}_2+\text{CH}_3\text{CH}_2\text{OH}$; (4) by the action of an acidyl chlorid upon dry ammonia. Thus, acetamid is produced by acetyl chlorid: $\text{CH}_3\text{CO.Cl}+2\text{NH}_3=\text{NH}_4\text{Cl}+\text{CH}_3\text{CO.NH}_2$.

The **secondary monamids** are obtained: (1) by the action of acidyl chlorids upon the primary monamids. Thus, diacetamid is produced from monacetamid: $\text{CH}_3\text{CO.NH}_2+\text{CH}_3\text{CO.Cl}=\text{HCl}+(\text{CH}_3\text{CO})_2\text{NH}$; (2) by the action of hydrochloric acid upon the primary monamids at high temperatures; $2(\text{CH}_3\text{CO.NH}_2)+\text{HCl}=\text{NH}_4\text{Cl}+(\text{CH}_3\text{CO})_2\text{NH}$.

The tertiary amids of this series have been imperfectly studied. Some have been obtained by the action of acidyl chlorids upon metallic derivatives of secondary amids: $(\text{CH}_3\text{CO})_2\text{NaN}+\text{CH}_3\text{CO.Cl}=(\text{CH}_3\text{CO})_3\text{N}+\text{NaCl}$; or by the union of anhydrides and nitrils at 200° (392° F.): $\text{CH}_3\text{CN}+(\text{CH}_3\text{CO})_2\text{O}=(\text{CH}_3\text{CO})_3\text{N}$.

The **primary monamids** of the fatty acids are solid, crystallizable, neutral in reaction, volatile without decomposition, mostly soluble in alcohol and ether, and mostly capable of uniting with acids to form compounds similar in constitution to the ammoniacal salts: $\text{H}_2\text{N.CO.CH}_3+\text{HNO}_3=(\text{H}_3\text{N.CO.CH}_3)\text{NO}_3$. They are capable of uniting with H_2O to form the ammoniacal salts of the corresponding acids: $\text{H}_2\text{N.CO.CH}_3+\text{H}_2\text{O}=\text{CH}_3\text{COO(NH}_4\text{)}$, and with the alkaline hydroxids to form the metallic salts of the corresponding acids and ammonia: $\text{H}_2\text{N.CO.CH}_3+\text{KHO}=\text{CH}_3\text{COOK}+\text{NH}_3$. They are converted into amines containing one atom of carbon less than themselves by the action of bromine and alkali (p. 379). The **secondary monamids**, containing two radicals of the fatty series, are acid in reaction, and their remaining atom of extra-radical hydrogen may be replaced by an electro-positive atom.

Formamid— CHO.NH_2 —45—is a colorless liquid, soluble in H_2O and in alcohol, boils at 192° – 195° (377.6° – 385° F.), suffering partial decomposition, obtained by heating ethyl formate with an alcoholic

solution of ammonia, or by the dry distillation of ammonium formate. It is decomposed by dehydrating agents, with formation of hydrocyanic acid: $\text{H}_2\text{N}(\text{H.CO})=\text{HCN}+\text{H}_2\text{O}$. Mercury formamid is obtained in solution by gently heating freshly-precipitated mercuric oxid with H_2O and formamid.

Under the name **chloralamid** a compound, formed by the union of chloral and formamid, and having the constitution, $\text{CCl}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{NH} \end{smallmatrix} .\text{CHO}$, has been used as a hypnotic. It forms colorless, odorless, faintly bitter crystals, fusible at 115° (239°F.), sparingly soluble in water. It is decomposed by alkalies, chloroform and ammonia being among the products of the decomposition. It is not affected by acids.

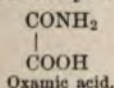
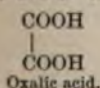
Chloralimid— $\text{CCl}_3.\text{C} \begin{smallmatrix} \text{NH} \\ \diagup \\ \text{H} \end{smallmatrix}$ —is another related derivative, formed by the action of ammonium acetate upon chloral hydrate, or by heating chloral ammonia. It is a crystalline solid, sparingly soluble in water, readily soluble in ether and in alcohol. When heated to 180° (365°F.) it is decomposed into chloroform and formamid.

Acetamid— $\text{CH}_3.\text{CO}.\text{NH}_2$ —is obtained by heating, under pressure, a mixture of ethyl acetate and ammonium hydroxid, and purifying by distillation. It is solid, crystalline, very soluble in H_2O , alcohol, and ether; fuses at 82° (179.6°F.); boils at 222° (431.6°F.); has a sweetish, cooling taste, and an odor of mice. Boiling potassium hydroxid solution decomposes it into potassium acetate and ammonia. Phosphoric anhydrid deprives it of H_2O , and forms with it **acetonitril** or **methyl cyanid**: $\text{H}_2\text{N.CO.CH}_3=\text{CH}_3.\text{CN}+\text{H}_2\text{O}$.

Alkyl-amids—are compounds similar in structure to the secondary and tertiary monamins and monamids, but containing both alkyls and acidyls. They are formed: (1) by the action of esters upon amins. Thus ethylacetamid is formed from ethyl acetate and ethylamin: $\text{CH}_3.\text{COO}(\text{C}_2\text{H}_5)+\text{H}_2\text{N}(\text{C}_2\text{H}_5)=(\text{CH}_3.\text{CO}).\text{HN}(\text{C}_2\text{H}_5)+\text{C}_2\text{H}_5.\text{OH}$; (2) from acidyl halids and amins: $\text{CH}_3.\text{COCl}+2\text{H}_2\text{N}(\text{C}_2\text{H}_5)=(\text{CH}_3.\text{CO}).\text{HN}(\text{C}_2\text{H}_5)+\text{ClH}_3\text{N}(\text{C}_2\text{H}_5)$; and $2\text{HN}(\text{C}_2\text{H}_5)_2+\text{CH}_3.\text{COCl}=(\text{CH}_3.\text{CO}).\text{N}(\text{C}_2\text{H}_5)_2+\text{ClH}_2\text{N}(\text{C}_2\text{H}_5)_2$; (3) from the isocyanids and fatty acids: $2\text{CH}_3.\text{COOH}+\text{CN}.\text{CH}_3=(\text{H.CO}).\text{HN}.\text{CH}_3+(\text{CH}_3.\text{CO})_2\text{O}$.

AMIDS OF DICARBOXYLIC ACIDS.

As the hydramins, the diamins (p. 382) and the imins (p. 387) are all derivable from the dihydric alcohols, by substitution of NH_2 for OH in the first, of 2NH_2 for 2OH in the second, and of NH for 2OH in the last, so amic acids, diamids, and imids are correspondingly derived from the dicarboxylic acids:



and, recognizing that carbonic acid is a pure dicarboxylic acid, although not a member of the oxalic series, we have:



Carbamic Acid—Amidoformic Acid— $\text{H}_2\text{N}.\text{CO}.\text{OH}$ —is not known in the free state, being decomposed into CO_2 and NH_3 , but ammonium carbamate is formed whenever ammonia and carbon dioxid are in contact: $\text{CO}_2 + 2\text{NH}_3 = \text{H}_2\text{N}.\text{CO}.\text{O}(\text{NH}_4)$, and it therefore exists in commercial ammonium carbonate, and is formed by oxidation of many carbon-nitrogen compounds, notably amido-acids, in alkaline solution. It exists normally in the blood and urine, and is formed in the system as an intermediate product between amido-acids and urea. It is obtained by directing dry ammonia and carbon dioxid into cold absolute alcohol, as a white, crystalline precipitate.

The esters of carbamic acid, called **urethans**, are more stable than its salts. They are formed by the action of ammonia upon the carbonic esters: $\text{OC}:(\text{OC}_2\text{H}_5)_2 + \text{NH}_3 = \text{H}_2\text{N}.\text{CO}.\text{O}(\text{C}_2\text{H}_5) + \text{CH}_3.\text{CH}_2\text{OH}$; and by the action of cyanogen chlorid upon alcohols: $\text{CNCl} + 2\text{CH}_3.\text{CH}_2\text{OH} = \text{H}_2\text{N}.\text{CO}.\text{O}(\text{C}_2\text{H}_5) + \text{CH}_3.\text{CH}_2\text{Cl}$. **Ethyl urethan**, produced by the above reactions, forms thin, large, transparent plates, f. p. 50° , b. p. 184° , very soluble in water and in alcohol. It is used as a hypnotic, either alone or combined with chloral in **uralium**, or **somnal**. **Phenyl urethan**, $\text{H}_2\text{N}.\text{CO}.\text{O}(\text{C}_6\text{H}_5)$, is a light, white powder, almost insoluble in water, very soluble in alcohol, which is used as an anti-pyretic under the name **euphorine**.

Carbamyl Chlorid—Urea Chlorid— $\text{H}_2\text{N}.\text{CO}.\text{Cl}$ —is formed by the interaction of carbonyl chlorid and ammonium chlorid at 400° : $\text{COCl}_2 + \text{NH}_4\text{Cl} = \text{H}_2\text{N}.\text{CO}.\text{Cl} + 2\text{HCl}$. It is a crystalline solid, f. p. 50° , b. p. 61° , at which latter temperature it dissociates to cyanic and hydrochloric acids: $\text{H}_2\text{N}.\text{CO}.\text{Cl} = \text{NCOH} + \text{HCl}$, and the former polymerizes to cyammelid (p. 396).

One or both of the H atoms of carbamyl chlorid may be replaced by alkyls to form **urea chlorids**, which are produced by the action of carbonyl chlorid upon the monamin hydrochlorids: $\text{ClH}_3\text{N}.(C_2\text{H}_5) + \text{COCl}_2 = (C_2\text{H}_5)\text{HN}.\text{CO}.\text{Cl} + 2\text{HCl}$, or $\text{ClH}_2\text{N}:(\text{CH}_3)_2 + \text{COCl}_2 = (\text{CH}_3)_2\text{N}.\text{CO}.\text{Cl} + 2\text{HCl}$.

Carbamyl chlorid and the urea chlorids are decomposed by water to CO_2 and ammonium chlorid or amin hydrochlorids: $\text{H}_2\text{N}.\text{CO}.\text{Cl} + \text{H}_2\text{O} = \text{CO}_2 + \text{NH}_4\text{Cl}$, or $(\text{CH}_3)\text{HN}.\text{CO}.\text{Cl} + \text{H}_2\text{O} = \text{CO}_2 + \text{ClH}_3\text{N}.\text{CH}_3$. They form urethans with alcohols: $\text{H}_2\text{N}.\text{CO}.\text{Cl} + \text{CH}_3.\text{CH}_2\text{OH} = \text{H}_2\text{N}.\text{CO}.\text{O}(\text{C}_2\text{H}_5) + \text{HCl}$. With amins they form alkyl ureas (p. 406): $\text{H}_2\text{N}.\text{CO}.\text{Cl} + \text{H}_2\text{N}.(C_2\text{H}_5) = \text{H}_2\text{N}.\text{CO}.\text{NH}(C_2\text{H}_5) + \text{HCl}$. In presence of Al_2Cl_6 they form amids with benzene and with phenol ethers (p. 446).

Oxamic Acid— $\text{COOH}.\text{CONH}_2$ —and its superior homologues are obtained by carefully distilling the monoammonium salt of the acid: $\text{COOH}.\text{COO}(\text{NH}_4)=\text{COOH}.\text{CONH}_2+\text{H}_2\text{O}$, a method of formation corresponding to those by which the monamids and diamids are produced. Or their salts are formed by the action of alkalies upon the imins. Thus succinamic acid is formed from succinimid: $\begin{matrix} \text{CH}_2.\text{CO} \\ \text{CH}_2.\text{CO} \end{matrix} \rangle \text{NH} + \text{KHO} = \text{H}_2\text{N}.\text{CO}.\text{CH}_2.\text{CH}_2.\text{COOK}$.

Malonamic Acid is unknown, although its ethyl ester: $\text{CONH}_2.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$, is known. **Succinamic Acid**, $\text{CONH}_2.\text{CH}_2.\text{CH}_2.\text{COOH}$, is obtained as described above. Its amido derivatives are the asparagins (p. 419).

Acids also exist, either as such or in their esters, in which one or both of the H atoms in NH_2 of carbamic, oxamic acid, etc., is or are replaced by alkyls. Such are ethyloxamic acid, $\text{COOH}.\text{CONH}(\text{C}_2\text{H}_5)$, and diethyloxamic ester, $\text{COO}(\text{C}_2\text{H}_5).\text{CON}(\text{C}_2\text{H}_5)_2$. These compounds correspond to the anilic acids of the cyclic series, such as oxanilic acid (p. 480): $\text{COOH}.\text{CONH}(\text{C}_6\text{H}_5)$.

The **primary diamids** only are acyclic compounds (see diamins, p. 385). They are formed: (1) by the action of ammonia upon the neutral esters. Thus ethyl oxalate yields oxamid: $\text{COO}(\text{C}_2\text{H}_5).\text{COO}(\text{C}_2\text{H}_5)+2\text{NH}_3=\text{CONH}_2.\text{CONH}_2+2\text{CH}_3.\text{CH}_2\text{OH}$; (2) by heating the neutral ammonium salt of the corresponding acid. Thus ammonium carbonate yields carbamid: $\text{OC}:(\text{ONH}_4)_2=\text{H}_2\text{N}.\text{CO}.\text{NH}_2+2\text{H}_2\text{O}$.

Carbamid—Urea— $\text{H}_2\text{N}.\text{CO}.\text{NH}_2$ —exists in the urine of mammalia, and, in smaller quantity, in the excrement of birds, fishes and some reptiles; also in the mammalian blood, chyle, lymph, liver, spleen, lungs, brain, vitreous and aqueous humors, saliva, perspiration, bile, milk, amniotic and allantoic fluids, and in serous fluids.

Urea is formed by the methods given above; also, (1) as a product of decomposition of uric acid, usually by oxidation. Thus nitric acid oxidizes uric acid to urea and alloxan: $2\text{C}_5\text{H}_4\text{N}_4\text{O}_3+2\text{H}_2\text{O}+\text{O}_2=2\text{CON}_2\text{H}_4+2\text{C}_4\text{H}_2\text{N}_2\text{O}_4$. (2) By the hydrolysis of creatin. Thus urea and sarcosin are formed by the action of KHO upon creatin: $\text{C}_4\text{H}_9\text{N}_3\text{O}_2+\text{H}_2\text{O}=\text{CON}_2\text{H}_4+\text{C}_3\text{H}_7\text{NO}_2$. (3) By the action of carbonyl chlorid upon dry ammonia: $\text{COCl}_2+2\text{NH}_3=\text{CON}_2\text{H}_4+2\text{HCl}$. (4) By the action of barium hydroxid upon guanidin (p. 388), or upon the hexon bases, lysin and arginin, products of decomposition of the proteins (p. 417). (5) By atomic transposition of its isomere, ammonium isocyanate, by heat: $\text{O}:\text{C}:\text{N}.\text{NH}_4=\text{H}_2\text{N}.\text{CO}.\text{NH}_2$. (6) By the action of ammonia upon phosgene or upon urea chlorids: $\text{COCl}_2+4\text{NH}_3=\text{H}_2\text{N}.\text{CO}.\text{NH}_2+2\text{NH}_4\text{Cl}$, or $\text{H}_2\text{N}.\text{CO}.\text{Cl}+2\text{NH}_3=\text{H}_2\text{N}.\text{CO}.\text{NH}_2+\text{NH}_4\text{Cl}$. (7) By heating ammonium carbamate to 130° : $\text{H}_2\text{N}.\text{CO}.\text{ONH}_4=\text{H}_2\text{N}.\text{CO}.\text{NH}_2+\text{H}_2\text{O}$. (8) By the action of ammonia upon urethan: $\text{H}_2\text{N}.\text{CO}.\text{O}(\text{C}_2\text{H}_5)+\text{NH}_3=\text{H}_2\text{N}.\text{CO}.\text{NH}_2+\text{CH}_3.\text{CH}_2\text{OH}$.

Urea crystallizes in long rhombic needles or prisms. It is colorless and odorless, and has a cooling taste, somewhat resembling that of saltpeter. It is neutral in reaction, although basic in character; soluble in one part of water, in five parts of cold alcohol, and in one part of boiling alcohol, sparingly soluble in amyl alcohol and in acetic ether, and still less soluble in ether. It fuses at 132° .

When heated a few degrees above its fusing point urea appears to boil, from escape of NH_3 , and is decomposed at about 140° with formation of ammeline (p. 537), $\text{C}_3\text{H}_4\text{N}_4\text{O}_2$; biuret (p. 407), $\text{C}_2\text{H}_5\text{N}_2\text{O}_2$, and cyanuric acid (pp. 396, 537), $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$, according to the equation: $8\text{H}_2\text{N}.\text{CO}.\text{NH}_2 = \text{H}_2\text{N}.\text{C} \begin{smallmatrix} \text{N.C}(\text{OH}) \\ \text{N.C}(\text{OH}) \end{smallmatrix} \text{N} + \text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2 + \text{HO}.\text{C} \begin{smallmatrix} \text{N.C}(\text{OH}) \\ \text{N.C}(\text{OH}) \end{smallmatrix} \text{N} + 6\text{NH}_3 + \text{H}_2\text{O}$. The ammeline formed is further hydrolysed by continued heating to cyanuric acid and ammonia: $\text{C}_3\text{H}_4\text{N}_4\text{O}_2 + \text{H}_2\text{O} = \text{C}_3\text{H}_3\text{N}_3\text{O}_3 + \text{NH}_3$, and finally at this temperature a dry solid residue remains, which, dissolved in water, gives the biuret reaction with CuSO_4 and KHO (p. 407). On continuing the heat to about 150° the biuret is also decomposed with evolution of ammonia, leaving cyanuric acid as the sole solid residue: $3\text{C}_2\text{H}_5\text{N}_2\text{O}_2 = 2\text{C}_3\text{H}_3\text{N}_3\text{O}_3 + 3\text{NH}_3$. Finally, if cyanuric acid be heated with alkalis it is slowly, but completely, hydrolysed to carbon dioxide and ammonia: $\text{C}_3\text{H}_3\text{N}_3\text{O}_3 + 3\text{H}_2\text{O} = 3\text{CO}_2 + 3\text{NH}_3$. Folin's quantitative method for urea (p. 714), in which the required temperature is attained by boiling MgCl_2 , 6Aq., b. p. 160° , is based upon these decompositions.

Dilute aqueous solutions of urea are not decomposed by boiling, but if the solution be concentrated, or, if the boiling be prolonged, or the temperature raised above 100° by pressure or otherwise, urea is partly or completely hydrolysed to CO_2 and NH_3 : $\text{H}_2\text{N}.\text{CO}.\text{NH}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{NH}_3$. Many hydrolysing agents, such as dilute acids or alkalis, BaH_2O_2 and BaCl_2 at a boiling temperature, BaCO_3 at 180° , and certain bacteria and enzymes bring about the same decomposition, which is that which occurs in "fermenting" urine.

Nitrous acid decomposes urea, as it does all aliphatic amines and amides, with evolution of the nitrogen from both acid and amide as free nitrogen: $\text{H}_2\text{N}.\text{CO}.\text{NH}_2 + 2\text{HNO}_2 = \text{CO}_2 + 2\text{N}_2 + 3\text{H}_2\text{O}$. A similar decomposition, but yielding half as much nitrogen per mol of urea, is effected by direct or indirect oxidants, such as alkaline solutions of hypochlorites and hypobromites, chlorin, etc.: $2\text{H}_2\text{N}.\text{CO}.\text{NH}_2 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{N}_2 + 4\text{H}_2\text{O}$.

With formic aldehyde urea forms a product, probably of condensation, whose constitution is still undetermined, which separates as a white, crystalline, almost insoluble solid when excess of formalin is added to solutions of urea containing a little HCl . When added to a concentrated solution of furfural and HCl , solid urea, or urea

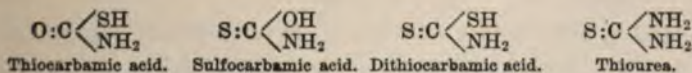
nitrate, forms a yellow solution, changing in color to green, blue and intense purple-violet; and after a time the mixture thickens and blackens (Schiff's reaction). Urea and amidoacetic acid, when fused together, combine, in part, to form uric acid: $3\text{H}_2\text{N.CO.NH}_2 + \text{CH}_2\text{-NH}_2\text{.COOH} = \text{C}_5\text{H}_4\text{N}_4\text{O}_3 + 2\text{H}_2\text{O} + 3\text{NH}_3$ (pp. 407, 529). With phenylhydrazin, urea in acetic acid solution condenses to phenylsemicarbazid: $\text{H}_2\text{N.CO.NH}_2 + \text{H}_2\text{N.NH.C}_6\text{H}_5 = \text{H}_2\text{N.CO.NH.NH.C}_6\text{H}_5 + \text{NH}_3$, a white, sparingly soluble, crystalline solid, f. p. 170° . With phosphotungstic acid, urea forms a compound of such solubility that a precipitate is formed if the proportion of urea be greater than 2 per cent, but none if it be less (p. 716). Urea is not precipitated from aqueous solutions containing BaCl_2 and BaH_2O_2 by a mixture of alcohol and ether 1:2 (p. 715).

Urea forms definite compounds, not only with acids, but also with certain salts and oxids. **Urea nitrate**— $\text{H}_2\text{N.CO.NH}_3\text{.NO}_3$ —forms, in white crystals, when a concentrated solution of urea is treated with nitric acid in the cold. It is much less soluble than urea, especially in presence of an excess of nitric acid. It is decomposed by evaporation of its solutions. **Urea oxalate**— $\text{CO}:(\text{NH}_3)_2:\text{O}_4\text{-C}_2$ —separates as a fine, crystalline powder, from mixed concentrated aqueous solutions of urea and oxalic acid. Its solution may be evaporated without decomposition.

When solutions containing molecular weights of urea and sodium chlorid are evaporated, prismatic crystals, containing CON_2H_4 , $\text{NaCl} + \text{H}_2\text{O}$ are obtained. Urea forms several compounds with mercuric oxid. Of these, the compound $(\text{CON}_2\text{H}_4)_2, 4\text{HgO}$, containing 72 parts of HgO for 10 parts of urea, is formed as a white, amorphous precipitate when a dilute solution of mercuric nitrate is gradually added to a dilute, alkaline solution of urea, and the excess of acid neutralized from time to time.

THIOUREA AND THIOCARBAMIC ACIDS.

The thio-compounds, corresponding to carbamic acid (p. 402) and to urea, in which oxygen is replaced by sulfur, exist either in their own forms or in their derivatives. Thus:



Thiocarbamic acid and **sulfocarbamic acid** are known only in their esters. **Dithiocarbamic acid** may be obtained by decomposition of its ammonium salt, which is produced by the action of ammonia in alcoholic solution upon carbon disulfid: $\text{CS}_2 + 2\text{NH}_3 = \text{S:C} \begin{array}{l} \text{S(NH}_4\text{)} \\ \text{NH}_2 \end{array}$.

Similarly, the amin salts of the alkyl-dithiocarbamic acids are formed by the action of the primary amins upon carbon disulfid (p. 380).

Thiourea is obtained by heating ammonium isothiocyanate: $\text{S}:\text{C}:\text{N}(\text{NH}_4)=\text{S}:\text{C}\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$, as urea is obtained from the isocyanate (p. 403). It is also formed by the action of hydrogen sulfid upon cyanamid (p. 398): $\text{H}_2\text{S}+\text{CN}.\text{NH}_2=\text{S}:\text{C}\begin{smallmatrix} \text{NH}_2 \\ \text{NH}_2 \end{smallmatrix}$. It is decomposed by boiling acids or alkalies into CO_2 , NH_3 , and H_2S . It forms salts, and alkyl, phenyl and acidyl derivatives similar to those of urea. By addition with alkyl halids thiourea forms salts of alkyl thiopseudoureas, corresponding to pseudourea (p. 389), which are used in certain cyclic syntheses (p. 523): $\text{H}_2\text{N}.\text{CS}.\text{NH}_2+\text{C}_2\text{H}_5\text{Cl}=\text{HN}:\text{C}\begin{smallmatrix} \text{NH}_2\text{Cl} \\ \text{S}.\text{C}_2\text{H}_5 \end{smallmatrix}$.

COMPOUND UREAS.

These compounds, which are exceedingly numerous, may be considered as derived from urea by the substitution of one or more alcoholic or acid radicals for hydrogen atoms.

Those containing alcoholic radicals, **alkyl ureas**, such as ethyl urea, $\text{CO}\begin{smallmatrix} \text{NH}_2 \\ \text{NH}.\text{C}_2\text{H}_5 \end{smallmatrix}$, are obtained: (1) By the action of primary or secondary amins upon isocyanic esters: $\text{NH}_2.\text{C}_2\text{H}_5+\text{O}:\text{C}:\text{N}.\text{C}_2\text{H}_5=\text{CO}:(\text{NH}.\text{C}_2\text{H}_5)_2$. (2) By heating the isocyanic esters with water, the amins and carbonic acid being formed as intermediate products: $\text{OC}:\text{N}.\text{C}_2\text{H}_5+\text{H}_2\text{O}=\text{NH}_2.\text{C}_2\text{H}_5+\text{CO}_2$, and $\text{OC}:\text{N}.\text{C}_2\text{H}_5+\text{NH}_2.\text{C}_2\text{H}_5=\text{CO}:(\text{NH}.\text{C}_2\text{H}_5)_2$. (3) By condensation of amins with urea chlorid (p. 402).

Those containing acid radicals have received the distinctive name of **ureïds**. Of these, some are **monureïds**, derived from a single molecule of urea, others **diureïds**, derived from two molecules. Some of the monureïds are open chain compounds, but the most important of them, and all the diureïds except carbonyl diurea are cyclic compounds, derivatives of glyoxalin, pyrimidin or cyanidin. Thus there are two ureïds, corresponding to glycollic acid, $\begin{smallmatrix} \text{CH}_2\text{OH} \\ | \\ \text{COOH} \end{smallmatrix}$: one, **hydantoïc acid**, an open chain ureïd: $\text{CO}\begin{smallmatrix} \text{NH}_2 \\ \text{NH}.\text{CH}_2.\text{COOH} \end{smallmatrix}$; the other, **hydantoïn**, a cyclic compound: $\text{CO}\begin{smallmatrix} \text{NH}.\text{CH}_2 \\ | \\ \text{NH}.\text{CO} \end{smallmatrix}$.

Only the acyclic ureïds will be here considered, the cyclic ones will be referred to as derivatives of their parent substances.

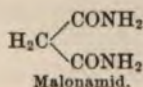
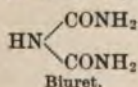
The **monacidyl monureïds**, containing a single acidyl, are formed by the action of acidyl chlorids or anhydrids upon urea. Thus acetyl-urea is obtained with acetyl chlorid: $\text{CH}_3.\text{CO}.\text{Cl}+\text{NH}_2.\text{CO}.\text{NH}_2=\text{H}_2\text{N}.\text{CO}.\text{NH}(\text{CO}.\text{CH}_3)+\text{HCl}$, or with acetic anhydrid: $(\text{CO}.\text{CH}_3)_2\text{O}+2\text{NH}_2.\text{CO}.\text{NH}_2=2\text{NH}_2.\text{CO}.\text{NH}(\text{CO}.\text{CH}_3)+\text{H}_2\text{O}$.

Mixed ureids, containing an alkyl and an acidyl, are formed in like manner from alkyl-ureas. Thus methyl-urea and acetyl chlorid form methyl-acetyl-urea: $\text{CH}_3.\text{NH}.\text{CO}.\text{NH}_2 + \text{CH}_3.\text{CO}.\text{Cl} = \text{CH}_3.\text{NH}.\text{CO}.\text{NH}(\text{CO}.\text{CH}_3) + \text{HCl}$. Such mixed ureids are also formed by the action of bromin and potassium hydroxid upon the amids, by reactions comparable with those which produce the monamins (p. 379). Thus methyl-acetyl-urea is formed from acetamid: $2\text{CH}_3.\text{CO}.\text{NH}_2 + \text{Br}_2 + 2\text{KHO} = \text{CH}_3.\text{HN}.\text{CO}.\text{NH}(\text{CO}.\text{CH}_3) + 2\text{KBr} + 2\text{H}_2\text{O}$.

The **diacidyl-ureids** are formed by the action of phosgene (carbonyl chlorid) upon the amids. Thus acetamid yields diacetyl-urea: $2\text{CH}_3.\text{CO}.\text{NH}_2 + \text{COCl}_2 = (\text{CH}_3.\text{CO})\text{HN}.\text{CO}.\text{NH}(\text{CH}_3.\text{CO}) + 2\text{HCl}$.

Allophanic acid— $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{COOH}$ —the simplest of the acyclic monureids, is that of carbonic acid, $\text{HO}.\text{CO}.\text{OH}$, and is known only in its esters.

Biuret— $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2$ —is both the amid of allophanic acid, and the monureid of carbamic acid, $\text{H}_2\text{N}.\text{CO}.\text{OH}$. It is formed by heating the allophanic esters with ammonia: $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{COO}-(\text{C}_2\text{H}_5) + \text{NH}_3 = \text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2 + \text{CH}_3.\text{CH}_2\text{OH}$; by condensation of urea and carbamic acid: $\text{H}_2\text{N}.\text{CO}.\text{NH}_2 + \text{HO}.\text{CO}.\text{NH}_2 = \text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2 + \text{H}_2\text{O}$; and by heating urea to about 150° : $2\text{H}_2\text{N}.\text{CO}.\text{NH}_2 = \text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CO}.\text{NH}_2 + \text{NH}_3$. When further heated it is itself decomposed to cyanuric acid and ammonia: $3\text{C}_2\text{H}_5\text{N}_3\text{O}_2 = 2\text{C}_3\text{H}_3\text{N}_3\text{O}_3 + 3\text{NH}_3$. It forms crystals, soluble in water, f. p. 190° . It is chiefly of interest in connection with the **biuret reaction**, which consists in the formation of a red-violet liquid when biuret is heated with a dilute solution of CuSO_4 alkalized with KHO (see Fehling's test). The reaction is due to the formation of a compound, $\text{Cu}[\text{NH}_2(\text{OH}).\text{CO}.\text{NH}.\text{CO}.\text{NH}_2-(\text{OH})\text{K}]_2$, which has been obtained in red crystals. Or NiSO_4 may be used in place of CuSO_4 , in which case an orange-colored liquid is produced. The biuret reaction is given by many substances other than biuret, such as malonamid, oxamid, aspartic diamid, albumins, albumoses, peptones, etc., and is considered to be proof of the presence in the substance giving it of two amido-carbonyl groups, CONH_2 , attached to each other, or to N or C, as in:



The reaction is also given by glycocol amid and sarcosin amid, which contain the grouping: $\text{H}_2\text{N}.\text{CH}_2.\text{CO}.\text{NH}_2$ (p. 578).

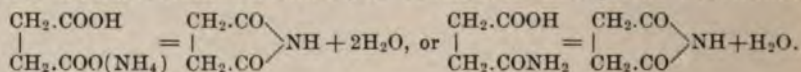
Hydantoic Acid—*Glycoluric Acid*— $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CH}_2.\text{COOH}$ —the next superior homologue of allophanic acid, is the acyclic monureid of glycollic acid, $\text{CH}_2\text{OH}.\text{COOH}$, and is obtained as its Ba salt by hydration of the corresponding cyclic monureid, hydantoin, by BaH_2O_2 (p. 515). It is also formed by condensation of urea and amido-

acetic acid at 120° : $\text{H}_2\text{N.CO.NH}_2 + \text{CH}_2\text{NH}_2.\text{COOH} = \text{H}_2\text{N.CO.NH.}-\text{CH}_2.\text{COOH} + \text{NH}_3$. (See also p. 405.)

Oxaluric Acid— $\text{H}_2\text{N.CO.NH.CO.COOH}$ —is the acyclic monureid of oxalic acid, and is obtained in its salts by hydration of those of the cyclic monureid, oxalylurea (p. 515). The free acid is a white, crystalline powder, sparingly soluble in water. It is easily further hydrolysed to urea and oxalic acid by heating with alkalies, or even with water. Its ammonium salt exists in the urine in small amount.

Carbonyl Diurea— $\text{H}_2\text{N.CO.NH.CO.HN.CO.NH}_2$ —the only acyclic diureid, is formed by the union of two urea molecules, with loss of H_2 , by the carbonyl group, brought about by the action of carbonyl chlorid upon urea: $2\text{H}_2\text{N.CO.NH}_2 + \text{COCl}_2 = \text{CO}(\text{HN.CO.NH}_2)_2 + 2\text{HCl}$. It is a sparingly soluble, crystalline powder, which is split by heat into cyanuric acid and ammonia: $\text{C}_3\text{H}_6\text{N}_4\text{O}_3 = \text{C}_3\text{H}_3\text{N}_3\text{O}_3 + \text{NH}_3$.

Imids are compounds derivable either by substitution of an acidylen for H_2 in a single NH_3 molecule, or by substitution of the imid group, NH , for $(\text{OH})_2$ in the carboxyls of a dicarboxylic acid (p. 401). They are obtained by the complete dehydration of the ammonium salts of the acids, or similarly from the amic acids (see pp. 400, 402). Thus monoammonic succinate, or succinamic acid yields succinimid:



The imids, therefore, except **carbimid**, corresponding to carbonic acid, which is isocyanic acid, O:C:N.H (p. 396), are heterocyclic compounds. The imids, when acted upon by alkalies or baryta water, produce the salts of the amic acids. Thus succinimid and caustic potash form potassium succinamate.

NITROGEN DERIVATIVES OF ALCOHOLS, ALDEHYDES AND KETONES.

Nitro derivatives of the alcohols, aldehydes, and ketones in which the NO_2 is substituted for OH or for O , such as $\text{CH}_3.\text{CH}_2(\text{NO}_2)$ and $\text{CH}_3.\text{CH}(\text{NO}_2)_2$ and $\text{CH}_3.\text{C}(\text{NO}_2)_2.\text{CH}_3$ are mono- or dinitro-paraffins (p. 376). Besides these, **nitro alcohols** are also known, in which the NO_2 is substituted in a hydrocarbon group, e. g., **nitro ethyl alcohol**, $\text{CH}_2(\text{NO}_2).\text{CH}_2\text{OH}$, which may also be considered as **nitro-hydrin**, corresponding to the chlorhydrin, $\text{CH}_2\text{Cl}.\text{CH}_2\text{OH}$.

Amido-alcohols, such as **amido ethyl alcohol**, or **oxethylamin**, $\text{CH}_2(\text{NH}_2).\text{CH}_2\text{OH}$, may also be considered as derived from the glycols by substitution of NH_2 for OH . These are the *oxyamins*, *hydroxamins*, *hydramins*, or *oxyamin bases*, among which are cholin and neurin (p. 382). By further substitution of NH_2 for OH they become *diamins* (p. 385).

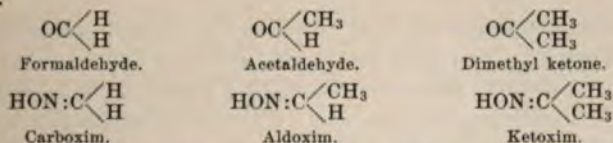
Aldehyde-ammonia—*Ethidene hydroxamin*— $\text{CH}_3.\text{CH} \begin{smallmatrix} \text{OH} \\ \text{NH}_2 \end{smallmatrix}$ —isomeric with ethylene hydroxamin, $\text{CH}_2(\text{NH}_2).\text{CH}_2\text{OH}$, may be considered as an amido ethyl alcohol in which the NH_2 is substituted for H in the methoxyl group, $\text{CH}_3.\text{CH}(\text{NH}_2)\text{OH}$. It is obtained by the action of dry NH_3 upon an ethereal solution of acetic aldehyde: $\text{CH}_3.\text{CHO} + \text{NH}_3 = \text{CH}_3.\text{CH}(\text{NH}_2)\text{OH}$. It is a crystalline solid, sparingly soluble in water, alkaline, f. p. 80° .

The corresponding compound derivable from formic aldehyde: $\text{H}.\text{CH}(\text{NH}_2)\text{OH}$, is not known; but when formaldehyde and ammonia react **hexamethylene tetramin**, $(\text{CH}_2)_6\text{N}_4$, is produced: $6\text{H}.\text{CHO} + 4\text{NH}_3 = (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O}$. This is a crystalline solid, very soluble in water, which decomposes when heated, and behaves as a monacid base. It is decomposed by weak acids and by acid salts, in the reverse manner to its formation, with liberation of formic aldehyde, a reaction which is probably caused by the acid sodium phosphate of the urine, and explains its action as a urinary antiseptic, for which purpose it is used under the names *formin* and *urotropin*.

Amido aldehydes, such as **amido acetaldehyde**, $\text{CH}_2(\text{NH}_2).\text{CHO}$, are also known.

Acetonamins.—The action of ammonia upon acetone causes a condensation of two or three molecules of acetone with one of ammonia, with formation of **diacetonamin**: $\text{CH}_3.\text{CO}.\text{CH} \begin{smallmatrix} \text{CH}_3 \\ (\text{CH}_3)_2 \end{smallmatrix} \text{C}.\text{NH}_2$, a colorless liquid; and **triacetonamin**: $\text{OC} \begin{smallmatrix} \text{CH}_2.\text{C}(\text{CH}_3)_2 \\ \text{CH}_2.\text{C}(\text{CH}_3)_2 \end{smallmatrix} \text{NH}$, a crystalline solid, f. p. 40° . Alkyl derivatives of these are formed when amins are used in place of ammonia. **Amido acetones**, or **amido ketones**, such as $\text{CH}_3.\text{CO}.\text{CH}_2(\text{NH}_2)$, **amido acetone**, are also known.

Aldoxims, and **ketoixims** or **acetoxims** are isomeric compounds derivable from the aldehydes and ketones by substitution of the **oxim** group, $=\text{N}.\text{OH}$, for oxygen. As the aldehydes and ketones are derivatives of formic aldehyde by substitution of alkyls for H, so the aldoixims and ketoixims are referable to **carboxim**, the oxim of formic aldehyde:



They are formed by the action of hydroxylamin upon aldehydes or ketones in alkaline solution, the aldoixims more readily than the ketoixims. Thus **acetaldoxim** is obtained from acetic aldehyde: $\text{CH}_3.\text{CHO} + \text{HONH}_2 = \text{CH}_3.\text{CH}:\text{NOH} + \text{H}_2\text{O}$, and **acetoxim** from dimethyl ketone: $\text{CH}_3.\text{CO}.\text{CH}_3 + \text{HONH}_2 = \text{CH}_3.\text{C}(\text{NOH}).\text{CH}_3 + \text{H}_2\text{O}$.

The aldoixims are colorless liquids, miscible with water; the

ketoxims crystalline solids, soluble in water. **Carboxim**, or **formoxim**, H.CH:NOH , b. p. 84° , polymerizes spontaneously to **triformoxim**; and is decomposed by boiling water to hydrocyanic acid and water.

Nascent hydrogen reduces both aldoxims and ketoxims to amins, those from the aldoxims being amins of primary alcohols and those from the ketoxims, amins of secondary alcohols: $\text{CH}_3.\text{CH:NOH} + 2\text{H}_2 = \text{CH}_3.\text{CH}_2\text{NH} + \text{H}_2\text{O}$, and $\text{CH}_3.\text{C}(\text{NOH}).\text{CH}_3 + 2\text{H}_2 = \text{CH}_3.\text{CHNH}_2.\text{CH}_3 + \text{H}_2\text{O}$. These reactions constitute a general method for obtaining amins (pp. 379, 382). Both aldoxims and ketoxims are hydrolysed to their parent substances by boiling with acids: $\text{CH}_3.\text{CH:NOH} + \text{H}_2\text{O} = \text{CH}_3.\text{CHO} + \text{HONH}_2$, and $\text{CH}_3.\text{C}(\text{NOH}).\text{CH}_3 + \text{H}_2\text{O} = \text{CH}_3.\text{CO}.\text{CH}_3 + \text{HONH}_2$.

The principal difference between aliphatic aldoxims and ketoxims is in their behavior towards acidyl halids and anhydrids, with which the former produce nitrils, and the latter esters. Thus with acetaldoxim: $\text{CH}_3.\text{CH:NOH} + \text{CH}_3.\text{COCl} = \text{CH}_3.\text{CN} + \text{CH}_3.\text{COOH} + \text{HCl}$, or $\text{CH}_3.\text{CH:NOH} + (\text{CH}_3.\text{CO})_2\text{O} = \text{CH}_3.\text{CN} + 2\text{CH}_3.\text{COOH}$; and with acetoxim: $(\text{CH}_3)_2\text{C:NOH} + \text{CH}_3.\text{COCl} = \text{CH}_3.\text{COO}[\text{N:C}:(\text{CH}_3)_2] + \text{HCl}$, or $(\text{CH}_3)_2\text{C:NOH} + (\text{CH}_3.\text{CO})_2\text{O} = \text{CH}_3.\text{COO}[\text{N:C}:(\text{CH}_3)_2] + \text{CH}_3.\text{COOH}$. Acetyl chlorid and anhydrid cause atomic rearrangement with acyclic and some higher aliphatic ketoxims, to form phenyl or alkyl amids: $\text{C}_6\text{H}_5\text{>C:NOH} = \text{C}_6\text{H}_5\text{>CH}_3.\text{CO>NH}$.

Aldehyde hydrazones and **ketone hydrazones** are compounds corresponding to the aldoxims and ketoxims, formed by condensation of the aldehydes and ketones with phenyl hydrazin (p. 484), the bivalent remainder of which, $=\text{N.NH.C}_6\text{H}_5$, is substituted for oxygen. They are obtained by the action of phenylhydrazin upon the aldehyde or ketone in ethereal solutions: $\text{CH}_3.\text{CHO} + \text{H}_2\text{N.NH.C}_6\text{H}_5 = \text{CH}_3.\text{CH}:(\text{N.NH.C}_6\text{H}_5) + \text{H}_2\text{O}$, or $(\text{CH}_3)_2\text{CO} + \text{H}_2\text{N.NH.C}_6\text{H}_5 = (\text{CH}_3)_2\text{C}:(\text{N.NH.C}_6\text{H}_5) + \text{H}_2\text{O}$.

NITROGEN DERIVATIVES OF ACIDS.

The nitrogen derivatives of the pure carboxylic acids are numerous and varied. They may be divided into two classes: (1) Those in which nitrogen or a nitrogen-containing group is substituted in the carboxyl for OOH or for OH, and (2) those in which the substitution is in a hydrocarbon group. The first class includes the nitrils, amidins, hydroxamic acids, amidoxims, nitrolic acids and amids, which have already been considered, and the **hydrazids**, which are compounds bearing the same relation to the hydrazins (p. 390) that the amids do to the amins.

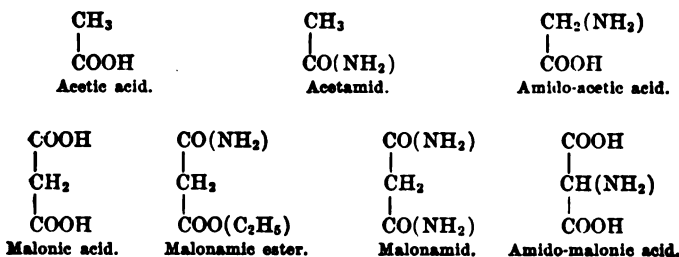
The following are included in the second class:

Nitro-acids, such as **nitro-acetic acid**, $\text{CH}_2(\text{NO}_2).\text{COOH}$, are un-

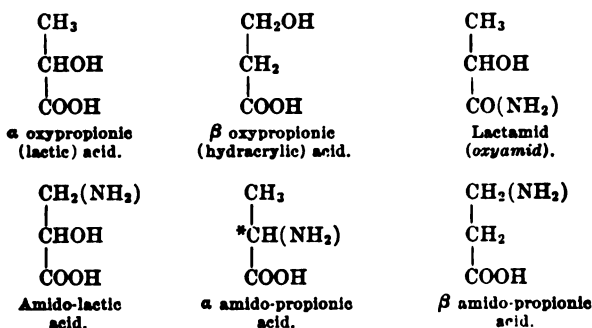
stable compounds, usually existing only in their esters and salts. As K salts they are obtained by the action of potassium nitrite upon the salts of the monochlor-fatty acids: $\text{CH}_2\text{Cl}.\text{COOK} + \text{KNO}_2 = \text{CH}_2(\text{NO}_2).\text{COOK} + \text{KCl}$. They are readily hydrolysed to nitroparaffins and a carbonate: $\text{CH}_2(\text{NO}_2).\text{COOK} + \text{H}_2\text{O} = \text{CH}_3.\text{NO}_2 + \text{KHCO}_3$.

Monamido-acids are much more stable, and include a number of substances of physiological interest. They are derived from the fatty acids by substitution of one NH_2 for a hydrogen atom in a hydrocarbon group. In this position the attachment of the amido group is much firmer than it is in the primary monamids, in which it replaces the hydroxyl. The amids are easily converted into ammonium salts by boiling water: $\text{H}_2\text{N}.\text{CO}.\text{CH}_3 + \text{H}_2\text{O} = \text{CH}_3.\text{COO}(\text{NH}_4)$; while the amido acids are not acted upon.

From the pure carboxylic acids (p. 327), amic acids (p. 401), or amids (p. 399) amido-acids are derivable by substitution of NH_2 for OH or for H:



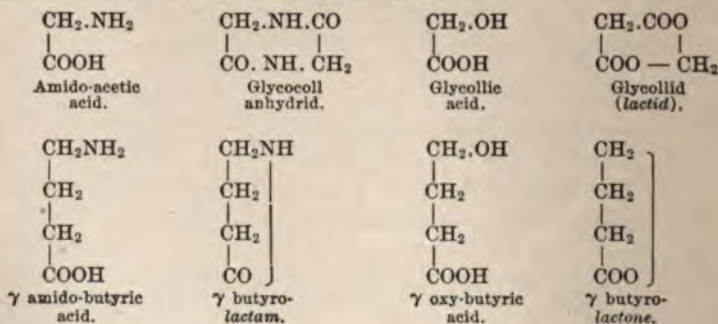
From the monocarboxylic oxyacids (p. 339), oxyamids are derived by substitution of NH_2 for OH in COOH ; amido-acids of the same series by its substitution for H in a hydrocarbon group; and amido-acids of the acetic series by its substitution for OH in a CHOH or a CH_2OH group:



The first amido-acid of the fatty series, amido-formic acid, $\text{NH}_2.\text{CO}.\text{OH}$, is carbamic acid (p. 402). The third and superior

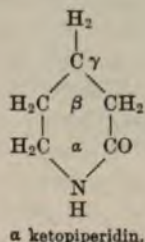
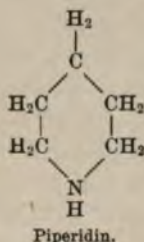
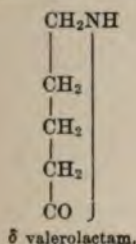
terms of the series form place isomeres, according to the position of the NH_2 group, corresponding to the oxyacids and similarly designated (p. 340) as α , β , γ , etc., or 1-, 2-, 3-, etc. Those acids in which the NH_2 is not attached to the terminal C atom contain an asymmetric C^* , and therefore exist in optical isomeres. The fatty amido-acids are also known as **glycocolls** or **alanins**. They are obtained: (1) By the action of ammonia upon the monochloro acids. Thus amido-acetic acid is obtained from monochloroacetic acid: $\text{CH}_2\text{Cl}.\text{COOH} + \text{NH}_3 = \text{CH}_2(\text{NH}_2).\text{COOH} + \text{HCl}$. (2) By reduction of the nitro-acids. Thus nitroacetic ester, $\text{CH}_2(\text{NO}_2).\text{COO}.\text{C}_2\text{H}_5$, yields amido-acetic ester. (3) By the action of nascent hydrogen upon the cyan-fatty acids: $\text{CN}.\text{COOH} + 2\text{H}_2 = \text{CH}_2(\text{NH}_2).\text{COOH}$.

The amido-acids are crystalline solids, most of which are sweet in taste, soluble in water, insoluble in alcohol or in ether, neutral in reaction. As they contain both amido and carboxyl groups, they have both basic and acid functions. With acids they form ammonium salts. They form stable metallic salts with bases, but their esters are unstable. The esters retain their basic function and form more stable hydrochlorids. Stable compounds are, however, produced by the replacement of their amido hydrogen, either by acidyls or by alkyls. The acidyl compounds, such as **acetyl amido-acetic acid**, $\text{CH}_2.\text{NH}(\text{C}_2\text{H}_3\text{O}).\text{COOH}$, are formed by the action of acidyl chlorids upon the amido-acids; and the alkyl derivatives, such as **methyl glycocoll**, $\text{CH}_2.\text{NH}(\text{CH}_3).\text{COOH}$, by the action of amins upon haloid fatty acids. On dehydration the amido-acids behave like the oxyacids (pp. 340, 368), which are also both basic and acid. The α acids on dehydration yield cyclic anhydrids, which are ketopiperazines (p. 522) and which on hydration yield, not two molecules of the acid, but a dipeptid (p. 416). The γ and δ acids yield cyclic esters, called **lactams**, corresponding to the lactones. The resemblance of these compounds is shown by the following formulæ:



The formation of the lactams is another instance of the production of closed chain from open chain compounds (pp. 368,

387). **Delta valerolactam** is the cyclic α keto-piperidin, or α -oxy-piperidin (p. 519):



By dry distillation the amido acids are split to amines and carbon dioxide: $\text{CH}_2\text{NH}_2.\text{COOH} = \text{CH}_3.\text{NH}_2 + \text{CO}_2$. When heated with hydriodic acid at 200° they are reduced to fatty acids: $\text{CH}_2\text{NH}_2.\text{COOH} + \text{H}_2 = \text{CH}_3.\text{COOH} + \text{NH}_3$. Amido acids of the acetic and oxalic series are converted into the corresponding monochlor acid by nitrosyl chloride: $\text{CH}_2\text{NH}_2.\text{COOH} + \text{NOCl} = \text{CH}_2\text{Cl}.\text{COOH} + \text{N}_2 + \text{H}_2\text{O}$. Nitrous acid acts upon the α -amido acids according to the reaction characteristic of the amido group (p. 380), converting them into oxyacids, with evolution of free nitrogen; $\text{CH}_2\text{NH}_2.\text{COOH} + \text{HNO}_2 = \text{CH}_2\text{OH}.\text{COOH} + \text{N}_2 + \text{H}_2\text{O}$. This conversion of amido into oxyacids, which probably occurs in the animal organism, is referred to as **deamidation**.

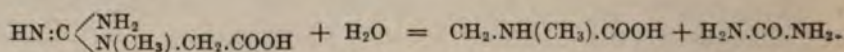
Amido-acetic Acid—Glycocoll—Glycin—Glycolamic acid—Gelatin sugar— $\text{CH}_2.\text{NH}_2.\text{COOH}$ —was first obtained by the action of H_2SO_4 upon gelatin. It is formed by the action of KHO upon glue; and, synthetically, by the methods given above and by the union of formic aldehyde, hydrocyanic acid and water: $\text{H}.\text{CHO} + \text{HCN} + \text{H}_2\text{O} = \text{CH}_2.(\text{NH}_2).\text{COOH}$. It is produced, along with benzoic acid, in the decomposition of hippuric acid (p. 479); as a product of decomposition of glycocholic acid; and by the action of hydriodic acid upon uric acid (p. 530). It occurs uncombined in the muscle of the scallop.

It appears as large, colorless, transparent crystals; has a sweet taste; fuses at 170° (338°F.); sparingly soluble in cold water; much more soluble in warm water; insoluble in absolute alcohol and in ether.

It forms crystalline salts with acids, which are decomposed at a boiling temperature. Nitric acid oxidizes it to glycollic acid. It is very resistant to oxidation by $\text{K}_2\text{Mn}_2\text{O}_8$ in acid solution, but in alkaline solution or in its esters it is readily oxidized to urea: $2\text{CH}_2\text{NH}_2.\text{COOH} + 3\text{O}_2 = \text{H}_2\text{N}.\text{CO}.\text{NH}_2 + 3\text{CO}_2 + 3\text{H}_2\text{O}$, from which it is presumed that the free acid does not exist as such, but as a lactam. Its acid function is more marked; it expels carbonic and acetic acids from calcium carbonate and lead acetate. It dissolves cupric hydroxid in alkaline solution, and there is no reduction on boiling the solution; but on addi-

tion of alcohol to the cold solution, blue crystalline needles of copper glycolamate separate. With ferric chlorid it gives an intense red color, which is discharged by acids, and restored by ammonia. With phenol and sodium hypochlorite it gives a blue color, as does ammonia. It forms esters and amids. Its methylic ester is isomeric with sarcosin. Heated under pressure with benzoic acid it forms hippuric acid. Fused with urea it forms glycolylurea (p. 515) and, ultimately, uric acid. Glycocoll may be separated from other amido acids by crystallization of the hydrochlorid of its ethyl ester.

Methyl-glycocoll—Sarcosin— $\text{CH}_2\text{NH}(\text{CH}_3)\text{COOH}$ —isomeric with alanin, the methyl ester of glycocoll, and lactamid, is not known to exist as such in animal nature, but it may be obtained from creatin (p. 389) by the action of barium hydroxid:



It is formed by the action of methylamin upon monochloroacetic acid: $\text{CH}_2\text{Cl.COOH} + \text{CH}_3\text{H}_2\text{N} = \text{CH}_2\text{NH}(\text{CH}_3)\text{COOH} + \text{HCl}$.

It crystallizes in colorless, transparent prisms; very soluble in water; sparingly soluble in alcohol and ether. Its aqueous solution is not acid, and has a sweetish taste. It forms salts with acids, but it is not known to form metallic salts. It unites with cyanamid to form creatin (p. 389); and with cyanogen chlorid to form methylhydantoin (p. 515).

Amido-propionic Acids—Alanins—Two are known: α alanin, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, formed by the reduction of α nitroso-propionic acid; and β alanin, $\text{CH}_2(\text{NH}_2)\text{CH}_2\text{COOH}$, formed either by the reduction of β nitroso-propionic acid, or by the action of ammonia upon β iodo-propionic acid. Neither is known to exist in nature. Nitrous acid converts the two alanins into the corresponding lactic acids.

Amido-butyric Acids— $\text{C}_4\text{H}_9\text{NO}_2$ —and **Amido-valerianic acids**— $\text{C}_5\text{H}_{11}\text{NO}_2$ —are mainly of theoretic interest. **Alpha amido-n-valerianic acid**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, is a product of oxidation of coniin. **Delta amido-n-valerianic acid—Butalanin**, $\text{CH}_2(\text{NH}_2)\text{CH}_2(\text{CH}_2)_3\text{COOH}$, occurs in the pancreas, and is formed as a product of decomposition of fibrin and of certain proteids.

Amido-caproic Acids—Leucins.—Twenty-nine isomeric amido acids are derivable from the seven caproic acids; and this number is still further increased by the fact that in many of these the introduction of the amido group renders a carbon atom asymmetric (see formula of α amido-propionic acid, p. 411). The leucin, which is of physiological interest as a product of decomposition of the proteins, is the inactive α amido-isobutyl-acetic acid, $(\text{CH}_3)_2\text{CH}.\text{CH}_2.*\text{CH}(\text{NH}_2).\text{COOH}$, as is demonstrated by its synthetic formation from

isovaleric aldehyde, $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CHO}$. The corresponding dextro-acid has been obtained by the action of *Penicillium glaucum* upon the inactive acid; and the lævo-acid, known as "vegetable leucin" from the vegetable globulin, conglutin.

"Animal leucin" is produced, accompanied by tyrosin (p. 478), in the decomposition of proteins by boiling with dilute acids or alkalies, by fusion with caustic alkalies, by putrefaction, and by trypsin digestion. It appears to exist also as a normal constituent of the pancreas, spleen, thymus, lymphatic and salivary glands, liver and kidneys. Pathologically the quantity of leucin is much increased in the liver in diseases of that organ, in typhus and in variola; in the bile in typhus; in the blood in leukæmia, and in yellow atrophy of the liver; in the urine in yellow atrophy of the liver, in typhus, in variola, and in phosphorus poisoning; in choleraic discharges from the intestine; in pus; in the fluids of dropsy and of atheromatous cysts. (See p. 756.)

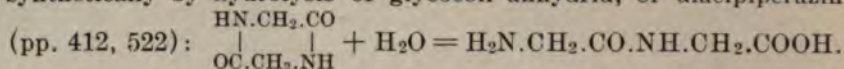
Leucin crystallizes from alcohol in soft, pearly plates, lighter than water, and somewhat resembling cholesterol; sometimes in rounded masses of closely grouped, radiating needles. Pure leucin is sparingly soluble in water, almost insoluble in alcohol and ether, but readily soluble in hot water or alcohol. When impure it is more soluble. It is odorless and tasteless, and its solutions are neutral. It dissolves readily in acids and alkalies, forming crystalline compounds with the former. It fuses and sublimates at 170° (338° F.) without decomposition, but at a slightly higher temperature is decomposed into amylamin and carbon dioxide.

When heated with hydriodic acid under pressure the leucins are decomposed into ammonia and the corresponding caproic acids. By nitrous acid they are oxidized to the corresponding **oxycaproic**, or **leucic acids**, $\text{C}_6\text{H}_{12}\text{O}_3$ (p. 342), with elimination of water and of nitrogen. Hot solutions of leucin form precipitates with hot solutions of cupric acetate. They dissolve cupric hydroxid, but do not reduce it on boiling. When boiled with solution of neutral lead acetate and carefully neutralized with ammonia, they deposit brilliant crystals of a compound of leucin and lead oxid. When HNO_3 is slowly evaporated in contact with leucin on platinum foil a colorless residue remains, which, when warmed with NaHO solution, turns yellow or brown, and on further concentration, forms oily drops, which do not adhere to the platinum (Scherer's reaction). Solution of leucin, when heated with solution of mercurous nitrate, liberates metallic mercury (Hofmeister's reaction).

Polypeptids—are products of tryptic digestion of proteins, intermediate between the peptones and amido-acids. They have been obtained synthetically by methods which show them to be constituted

by substitution of amido-acid radicals for H in NH_2 of the α -amido-acids. They are **dipeptids**, containing one such radical, or **tri-, tetra-, pentapeptids**, containing two, three and four.

Glycylglycin—is the simplest of these compounds. It is obtained synthetically by hydrolysis of glycocoll anhydrid, or diacipiperazin



Similarly other dipeptids containing like radicals: **alanylalanin**, **leucylleucin**, are obtained from other diacipiperazins.

Another method of synthesis permits of the formation of "mixed" polypeptids, as well as of those containing like radicals: By the action of chloracetyl chlorid upon α -alanin, chloracetyl-alanin is formed: $\begin{array}{c} \text{H}_3\text{C} \\ \text{H}_2\text{N} \end{array} \text{CH} \cdot \text{COOH} + \text{ClCH}_2 \cdot \text{CO} \cdot \text{Cl} = \begin{array}{c} \text{H}_3\text{C} \\ \text{ClCH}_2 \cdot \text{CO} \cdot \text{HN} \end{array} \text{CH} \cdot \text{COOH} +$

HCl . This is amidated by ammonia to **glycylalanin**: $\begin{array}{c} \text{H}_3\text{C} \\ \text{ClCH}_2 \cdot \text{CO} \cdot \text{HN} \end{array} \text{CH} \cdot \text{COOH} + 2\text{NH}_3 = \begin{array}{c} \text{H}_3\text{C} \\ \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \end{array} \text{CH} \cdot \text{COOH} + \text{NH}_4\text{Cl}$. This method of synthesis also permits of the formation of tri-, tetra-, and pentapeptids by repetition of the processes. Thus glycocoll and chloracetyl chlorid yield chloracetyl glycine: $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{COOH} + \text{ClCH}_2 \cdot \text{CO} \cdot \text{Cl} = \text{ClCH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + \text{HCl}$; and this is amidated by ammonia to **glycylglycin**: $\text{ClCH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + 2\text{NH}_3 = \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + \text{NH}_4\text{Cl}$. Glycylglycin with chloracetyl chlorid yields chloracetyl-glycylglycin: $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + \text{ClCH}_2 \cdot \text{CO} \cdot \text{Cl} = \text{ClCH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + \text{HCl}$; which is in turn amidated by ammonia to **diglycylglycin**: $\text{ClCH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + 2\text{NH}_3 = \text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{HN} \cdot \text{CH}_2 \cdot \text{COOH} + \text{NH}_4\text{Cl}$; and so on by successive steps to **tetraglycylglycin**: $\text{H}_2\text{N} \cdot (\text{CH}_2 \cdot \text{CO} \cdot \text{HN})_4 \cdot \text{CH}_2 \cdot \text{COOH}$. Curtius' base, a product of tryptic digestion, is probably **hexaglycylglycin ester**, $\text{H}_2\text{N} \cdot (\text{CH}_2 \cdot \text{CO} \cdot \text{NH})_6 \cdot \text{CH}_2 \cdot \text{COO}(\text{C}_2\text{H}_5)$.

These syntheses indicate the great reactivity of the amido group in these compounds, because of which, also, numerous products of substitution are known, and the esters, like those of the parent amido-acids, tend to form cyclic products of condensation. Diglycylglycin forms a condensed product which gives the biuret reaction, which is also given by triglycylglycin and the higher polypeptids.

Polypeptids are also formed with other amido-acids, aspartic acid, cystin, phenylalanin, tyrosin, and with prolin (p. 511).

Diamido Fatty Acids.—These compounds contain two amido groups, attached to two different carbon atoms. Attempts to obtain diamido acetic acid, $\text{CH}(\text{NH}_2)_2 \cdot \text{COOH}$ have been unsuccessful, and it is assumed that in these acids the two NH_2 groups are always attached to different carbon atoms, although the same prohibition in this regard

does not in general apply to the NH_2 group as it does to the OH group (p. 269), as is shown by the existence of urea and guanidin. The lowest term of the series is diamidopropionic acid; above this there may exist isomeres, increasing in number with increase in the number of carbon atoms, dependent upon the relative positions of the amido groups to the carboxyl.

They are formed as hydrobromids, by the action of ammonia upon the corresponding dibromo fatty acids. Thus α - β dibromopropionic acid yields α - β diamidopropionic acid hydrobromid: $\text{CH}_2\text{Br}.\text{CHBr}.\text{COOH} + 2\text{NH}_3 = \text{CH}_2\text{NH}_2.\text{CHNH}_2.\text{COOH}$. From the hydrobromids or hydrochlorids the free acids are liberated by an equivalent amount of AgHO . They are also obtained by a rather intricate synthesis, beginning with alkyl-malonic derivatives of phthalimid (p. 477).

They are syrups, or very hygroscopic crystals; strongly alkaline and basic, absorbing CO_2 from air, and forming crystalline salts. With benzoyl chlorid they form mono- and dibenzoyl derivatives, some of which exist in nature. They form crystalline precipitates with phosphotungstic acid, containing an asymmetric carbon atom; they exist in optical isomeres.

The diamido acids are chiefly of interest in connection with the **hexon bases**, which are basic substances formed during the development of lupine seeds, and by hydrolysis of proteins and of protamins (p. 588), containing six carbon atoms, and either being themselves, or yielding on decomposition, acids of this class: **Arginin**, $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$, a derivative of diamidovalerianic acid (below), **lysin**, $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$, which is a diamidocaproic acid (below), and **histidin**, $\text{C}_6\text{H}_9\text{N}_3\text{O}_2$, which is probably a glyoxalin derivative (p. 516). The name **hexone** is applied to all basic, nitrogenous C_6 compounds formed under the above conditions, and includes leucin as well as the hexon bases.

Diamidopropionic Acid— $\text{CH}_2\text{NH}_2.\text{CHNH}_2.\text{COOH}$ —is obtained as above indicated. Gaseous HNO_2 converts it into glyceric acid: $\text{CH}_2\text{NH}_2.\text{CHNH}_2.\text{COOH} + 2\text{HNO}_2 = \text{CH}_2\text{OH}.\text{CHOH}.\text{COOH} + 2\text{N}_2 + 2\text{H}_2\text{O}$, while the less intense action of AgNO_2 converts it into isoserin (p. 420): $\text{CH}_2\text{NH}_2.\text{CHNH}_2.\text{COOH} + \text{AgNO}_2 = \text{CH}_2\text{NH}_2.\text{CHOH}.\text{COOH} + \text{N}_2 + \text{AgHO}$.

Diamidobutyric Acids.—Two are possible, derived from the normal butyric acid, and two from the iso acid. The α - γ normal acid: $\text{CH}_2\text{NH}_2.\text{CH}_2.\text{CHNH}_2.\text{COOH}$, has been obtained synthetically.

Diamidovalerianic Acids.—Fourteen are possible, derivable from the four valerianic acids. Of these the α - δ -normal acid: $\text{CH}_2\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{CHNH}_2.\text{COOH}$, which has also been obtained synthetically, is the base **ornithin**, as is proven by its method of synthesis, and by the fact that under the influence of bacterial action it forms putrescin: $\text{CH}_2\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{CHNH}_2.\text{COOH} = \text{H}_2\text{N}.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.$

$\text{NH}_2 + \text{CO}_2$. Ornithin was first obtained by hydrolysis of its dibenzoyl derivative, **ornithuric acid**, which occurs in the urine of hens fed with benzoic acid (p. 480). Another diamidovalerianic acid has been obtained synthetically, which, being optically inactive, is probably the racemic form of ornithin, which is itself dextrogyrous $[\alpha]_D = +7.85^\circ$.

Arginin— $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$ —is the most abundant of the hexon bases. It was first obtained from the seeds of *Lupinus albus*, in which it exists preformed, and from which about 3.5 per cent can be extracted by water. Subsequently it was found to be produced, in larger proportion than lysin or histidin, by hydrolysis of proteins and protamins by boiling with $\text{HCl} + \text{SnCl}_2$, and also by tryptic digestion of fibrin.

The constitution of arginin is established by its decomposition products and synthesis. When hydrolysed by BaH_2O_2 , it yields urea and ornithin: $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH}_2 + \text{CH}_2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$. Conversely, it is obtained by partial synthesis from ornithin and cyanamid: $\text{CH}_2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH} + \text{CN} \cdot \text{NH}_2 = \text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$. This synthesis closely resembles that by which creatin (methylguanidin acetic acid) is produced from methylamidoacetic acid and cyanamid: $\text{CH}_2\text{NH}(\text{CH}_3) \cdot \text{COOH} + \text{CN} \cdot \text{NH}_2 = \text{HN} : \text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{N}(\text{CH}_3) \end{smallmatrix} \cdot \text{CH}_2 \cdot \text{COOH}$. Among the products of oxidation of arginin by various oxidants are: α -amidovalerianic acid: $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$; γ -guanidinbutyric acid: $\text{HN} : \text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$; ethylene-succinic acid: $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$; and guanidin: $\text{HN} : \text{C} : (\text{NH}_2)_2$. The structural formula of arginin is therefore: $\text{HN} : \text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$, and it is α -amido- δ -guanidin valerianic acid. It may also be considered as a product of condensation of urea and α - δ -diamidovalerianic acid: $\begin{smallmatrix} \text{H}_2\text{N} \\ \diagup \\ \text{H}_2\text{N} \end{smallmatrix} \text{CO} + \text{CH}_2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH} = \begin{smallmatrix} \text{H}_2\text{N} \\ \diagup \\ \text{HN} \end{smallmatrix} \text{C} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH} + \text{H}_2\text{O}$.

Arginin crystallizes in plates or prisms, f. p. 207° , odorless, slightly bitter, strongly alkaline, absorbs CO_2 from air, precipitates oxids from solutions of metallic salts, and expels NH_3 from ammoniacal salts, easily soluble in water, almost insoluble in alcohol.

Diamidocaproic Acids.—There are forty-nine possible diamido acids derivable from the seven caproic acids. Of these **lysin**, one of the hexon bases, is the α - ϵ -normal acid: $\text{CH}_2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$, as is shown by its conversion into pentamethylene diamine (cadaverin) by bacterial action: $\text{CH}_2\text{NH}_2 \cdot (\text{CH}_2)_3 \cdot \text{CHNH}_2 \cdot \text{COOH} = \text{H}_2\text{N} \cdot (\text{CH}_2)_5 \cdot \text{NH}_2 + \text{CO}_2$; and by its synthesis from γ -cyanopropylmalonic ester: $\text{NC} \cdot (\text{CH}_2)_3 \cdot \text{CH}(\text{COO} \cdot \text{C}_2\text{H}_5)_2$. It is probable that lysin

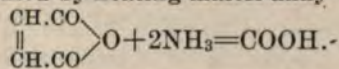
may form a guanidin derivative, similar to arginin, but it is still unknown. On the other hand, its dibenzoyl derivative, **lysuric acid**, corresponding to ornithuric and hippuric acids, has been obtained by the action of benzoyl chlorid upon lysin.

The supposed hexon base **lysatinin** is a mixture of arginin and lysin.

Amido-dicarboxylic Acids are derived from the dicarboxylic acids by substitution of NH_2 in a hydrocarbon group. The lowest term is therefore: **Amido-malonic Acid**— $\text{COOH.C}^*\text{H.NH}_2.\text{COOH}$ —a synthetic product, obtained by the reduction of nitrosomalonic acid: $\text{COOH.CH(NO).COOH} + 2\text{H}_2 = \text{COOH.CHNH}_2.\text{COOH} + \text{H}_2\text{O}$, which decomposes easily to amido-acetic acid and carbon dioxid: $\text{COOH.CHNH}_2.\text{COOH} = \text{CH}_2\text{NH}_2.\text{COOH} + \text{CO}_2$.

Amido-succinic Acid—Aspartic Acid— $\text{COOH.C}^*\text{H.NH}_2.\text{CH}_2.\text{COOH}$.—The lævo acid is produced during tryptic digestion of proteins, and is a product of their hydrolysis by dilute acids. It exists in beet-root vinasse, and is obtained from many vegetable substances as a product of decomposition of its amid, asparagin. It crystallizes in rhombic prisms, difficultly soluble in cold water, readily soluble in hot water. Nitrous acid converts it into l-malic acid: $\text{COOH.C}^*\text{H.NH}_2.\text{CH}_2.\text{COOH} + \text{HNO}_2 = \text{COOH.C}^*\text{H.OH.CH}_2.\text{COOH} + \text{N}_2 + \text{H}_2\text{O}$. It forms a crystalline compound with cupric oxid, which is soluble in hot water, but almost insoluble in cold water.

Asparagins,—Amido-succinamic Acids,—Amido-succinic Amids.—Two monamids are derivable from aspartic acid or from succinamic acid (p. 403): α -asparagin, $\text{CONH}_2.\text{C}^*\text{H.NH}_2.\text{CH}_2.\text{COOH}$, and β -asparagin, $\text{COOH.C}^*\text{H.NH}_2.\text{CH}_2.\text{CONH}_2$, each of which occurs in optical isomeres. The β -amid exists in both d- and l-forms in many plants, in asparagus and in the sprouts of vetches, beans and peas. The l-form, which predominates in nature, crystallizes in prisms, sparingly soluble in water, odorless, faintly nauseous in taste, faintly acid in reaction. The d- β -amid is also formed by heating maleïc anhydrid (p. 430), with alcoholic ammonia:



$\text{CHNH}_2.\text{CH}_2.\text{CONH}_2$. Asparagins enter into unstable combination with both bases and acids. Hydrolysed by acids or alkalies they form aspartic acid: $\text{COOH.CHNH}_2.\text{CH}_2.\text{CONH}_2 + \text{H}_2\text{O} = \text{COOH.CHNH}_2.\text{CH}_2.\text{COOH} + \text{NH}_3$. Nitrous acid converts them into malic acid: $\text{COOH.CHNH}_2.\text{CH}_2.\text{CONH}_2 + 2\text{HNO}_2 = \text{COOH.CHOH.CH}_2.\text{COOH} + 2\text{N}_2 + 2\text{H}_2\text{O}$.

Amido-glutaric Acid,—Glutaminic Acid.—The d-acid, which accompanies aspartic acid as a product of decomposition of the proteins and in the vegetables mentioned, is the d- α -acid: $\text{COOH.CH}_2.\text{CH}_2.$

$C^*H_2NH_2.COOH$. The β -acid, $COOH.CH_2.CHNH_2.CH_2.COOH$, which would not form optical isomeres, does not appear to exist. The α -acid crystallizes in rhombic octahedra, soluble in hot water, insoluble in alcohol and ether. The d-acid is produced by hydrolysis of proteins by acids; but the i-acid is formed when BaH_2O_2 is the hydrolysing agent. It forms a crystalline compound with HCl , which is almost insoluble in the concentrated acid. It forms a crystalline copper salt. **Glutamin**, or α -amidoglutaric- α -amid: $COOH.CH_2.CH_2.C^*H_2NH_2.CONH_2$, in the i-form, accompanies asparagin in the vegetables in which it occurs.

Monamido-oxyacids—are derivable from oxyacids by substitution of NH_2 for H in a hydrocarbon group, or for alcoholic OH in acids containing more than one such group.

Amido-lactic Acids, —Amido-glyceric Acids.—Corresponding to glyceric acid: $CH_2OH.C^*HOH.COOH$, are two monamido acids: $\alpha=CH_2OH.C^*H_2NH_2.COOH$, and $\beta=CH_2NH_2.C^*HOH.COOH$. The former is also **amidohydracrylic**, or α -amido- β -oxypropionic acid, and the latter **amido-lactic**, or α -oxy- β -amidopropionic acid. The α -amido acid is **serin**, a product of decomposition of **sericin** and **fibroin**, constituents of silk, and of other proteids. It has been obtained synthetically from glycollic aldehyde and hydrocyanic acid: $CH_2OH.CHO + CNH + H_2O = CH_2OH.CHNH_2.COOH$. Another total synthesis is from formic ester and hippuric ester (p. 479), which are first condensed to formylhippuric ester: $H.COO(C_2H_5) + CH_2(NH.CO.C_6H_5).COO(C_2H_5) = CHO.CH(NH.CO.C_6H_5).COO(C_2H_5) + CH_3.CH_2OH$; this is then reduced to monobenzoyl-serin ester, which by hydrolysis yields serin: $CH_2OH.CH(NH.CO.C_6H_5).COO(C_2H_5) + 2H_2O = CH_2OH.CHNH_2.COOH + C_6H_5.COOH + CH_3.CH_2OH$. The β -acid is **iso-serin**, obtained by the action of ammonia upon β -chlorlactic acid: $CH_2Cl.CHOH.COOH + NH_3 = CH_2NH_2.C^*HOH.COOH + HCl$. Serin on reduction by HI yields ordinary alanin: $CH_2OH.CHNH_2.COOH + H_2 = CH_3.CHNH_2.COOH + H_2O$, while isoserin yields β -amidopropionic acid: $CH_2NH_2.CHOH.COOH + H_2 = CH_2NH_2.CH_2.COOH + H_2O$. By the action of nitrous acid both are converted into glyceric acid: $CH_2OH.CHNH_2.COOH + HNO_2 = CH_2OH.CHOH.COOH + N_2 + H_2O$.

α -**Amido- γ -oxyvalerianic Acid** is formed from hydrocyanic acid and secondary aldol: $CNH + CH_3.CHOH.CH_2.CHO + H_2O = CH_3.C^*HOH.CH_2.C^*H_2NH_2.COOH$.

Glucosamic Acid — Tetroxy- α -amidocaproic Acid — $CH_2OH.(CHOH)_3.CHNH_2.COOH$ —corresponding to glucosamin (p. 387), has been obtained from cartilage.

Amido acids corresponding to the aldehyde acids and the ketone acids are not known, although α -amido-acetoacetic ester: $CH_3.CO.CHNH_2.COO(C_2H_5)$, has been obtained.

Amido-thioacids.—The following amido derivatives of thioacids are of physiological interest:

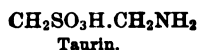
Amido-isethionic Acid, —Amido-ethylsulfonic Acid, —Taurin, —
 $\text{CH}_2\text{NH}_2.\text{CH}_2\text{SO}_3\text{H}$ —or $\begin{array}{c} \text{CH}_2.\text{NH}_3 \\ | \\ \text{CH}_2.\text{SO}_3 \end{array}$ the amido derivative of isethionic, or oxyethyl sulfonic acid (p. 372), $\text{CH}_2\text{OH}.\text{CH}_2\text{SO}_3\text{H}$, occurs in bile, in combination with cholic acid, as **taurocholic acid**, from which it may be obtained by decomposition by HCl . It is also produced by decomposition of amido-sulfopropionic acid, a product of oxidation of protein cystin: $\text{COOH}.\text{CHNH}_2.\text{CH}_2\text{SO}_3\text{H} = \text{CO}_2 + \text{CH}_2\text{NH}_2.\text{CH}_2\text{SO}_3\text{H}$. It is formed synthetically by heating together chlorethylsulfonic acid and ammonia: $\text{CH}_2\text{Cl}.\text{CH}_2\text{SO}_3\text{H} + \text{NH}_3 = \text{CH}_2\text{NH}_2.\text{CH}_2\text{SO}_3\text{H} + \text{HCl}$; or by heating ammonium oxethylsulfonate: $\text{CH}_2\text{OH}.\text{CH}_2.\text{SO}_3(\text{NH}_4) = \text{CH}_2\text{NH}_2.\text{CH}_2.\text{SO}_3\text{H} + \text{H}_2\text{O}$.

Taurin crystallizes in large, oblique rhombic prisms, soluble in water, insoluble in alcohol and ether. It appears in the urine partly in its own form, and partly combined with carbamic acid as **taurocarbamic acid**: $\text{H}_2\text{N}.\text{CO}.\text{NHCH}_2.\text{CH}_2\text{SO}_3\text{H}$. It also combines with sodium cholate to form taurocholic acid (p. 640). It differs from other amido acids in that it forms no salts with acids, and forms neither benzoyl nor acetyl derivative, which facts point toward the cyclic salt constitution shown in the second formula above. Its acid function is more marked. It forms compounds with metallic oxids. That of mercury is formed by boiling taurin solution with freshly precipitated mercuric oxid, and is white and insoluble. Taurin and cyanamid combine to form **taurocyanamin**, or **tauroglycocyanamin**, corresponding to creatin (p. 389): $\text{CH}_2\text{NH}_2.\text{CH}_2\text{SO}_3\text{H} + \text{H}_2\text{N}.\text{CN} = \text{HN}:\text{C} \begin{array}{l} \text{NH}_2 \\ \text{NH} \end{array} \text{CH}_2.\text{CH}_2\text{SO}_3\text{H}$. Nitrous acid converts it into isethionic acid: $\text{CH}_2\text{NH}_2.\text{CH}_2\text{SO}_3\text{H} + \text{HNO}_2 = \text{CH}_2\text{OH}.\text{CH}_2\text{SO}_3\text{H} + \text{N}_2 + \text{H}_2\text{O}$. Its sulfur is not split off by boiling alkaline solutions, but it is by fusion with caustic potash: $\text{CH}_2\text{NH}_2.\text{CH}_2\text{SO}_3\text{H} + 2\text{KHO} = \text{CH}_3.\text{COOH} + \text{K}_2\text{SO}_3 + \text{NH}_3 + \text{H}_2$.

Amido-thiolactic Acids.—Of the two possible thioacids corresponding to serin and isoserin (p. 420) that derivable from the former and from hydraacrylic, or β -lactic, acid, is known as **cystein**, which is α -amido- β -thiolactic acid (formula, p. 422). Cystein is obtained by the action of nascent hydrogen upon cystin, and is formed by an additional step to the synthesis of serin: the benzoyl-serin ester (p. 420) is converted into cystein by P_2S_5 . When oxidized by Br . it produces **cysteic acid**, or α -amido- β -sulfopropionic acid, which, although containing both sulfonic and carboxyl groups, is monobasic. Cystein forms benzoyl and alkyl and phenyl derivatives, the latter by substitution for H in SH . Although cystein is not produced by

hydrolysis of proteins, in which the S exists in cystin, not in cystein, it is eliminated in a "protected" form of combination by dogs after administration of benzene halids. These compounds, in which the phenylene-halid group takes the place of H in HS, and acetyl is substituted for H in NH₂, are called **mercapturic acids**. Cysteic acid by loss of CO₂ forms taurin.

Cystin, which is α -diamido— β -dithiodilactic acid, occurs in urinary sediments and calculi, and is formed by hydrolysis of many proteins, in greatest abundance from hair, horns, hoofs, and is similarly produced in the system and appears in the urine in "cystinuria." It crystallizes in thin, six-sided plates, insoluble in water, alcohol, ether, or acetic acid, soluble in mineral acids and alkalies.



PHOSPHORUS, ANTIMONY, AND ARSENIC DERIVATIVES.

Many organic compounds, similar to those containing nitrogen, in which that element is replaced by phosphorus, antimony, or arsenic, are known. Of these only a few arsenic derivatives require mention.

Dimethyl Arsin—(CH₃)₂HAs—corresponding to dimethyl amin, (CH₃)₂HN, is a colorless liquid, having an intensely disagreeable odor, which ignites spontaneously in air. It may be considered as the hydrid of a radical, (CH₃)₂As, which, from the disagreeable odor and intensely poisonous action of all of its compounds, has received the name **cacodyl** (κακός=evil). As the amins are considered as derived from ammonia by substitution of alkyl groups for the hydrogen, so the compounds of which this is a type are derived from the corresponding hydrogen compounds of phosphorus, antimony, and arsenic, and are called **phosphins**, **stibins**, and **arsins**.

The parent substance of the arseno-organic compounds is a fuming, foul-smelling liquid, obtained by distilling a mixture of arsenic trioxid and potassium acetate, and called **fuming liquid of Cadet**. The principal constituent of this is **cacodyl oxid**, or **alkarsin**, $\begin{matrix} (\text{CH}_3)_2\text{As} \\ (\text{CH}_3)_2\text{As} \end{matrix} \text{O}$, a liquid which boils at 120° (248° F.), insoluble in water, soluble in alcohol and in ether. **Cacodyl**, or **dicacodyl**, (CH₃)₂ As.-As(CH₃)₂ is a colorless, insoluble liquid, which boils at 170° (338° F.), and ignites spontaneously in air. Cacodyl and all of its compounds

are exceedingly poisonous, especially the cyanid, an ethereal, volatile liquid the presence of whose vapor in air, even in minute traces, produces symptoms referable both to arsenic and to cyanogen. Probably minute quantities of arsins are formed during the putrefaction of cadavers embalmed with arsenical liquids.

UNSATURATED ALIPHATIC COMPOUNDS.

In this class are included all open chain carbon compounds in which two carbon atoms exchange more than one valence (p. 268). As the saturated compounds consist of the members of the first, or methane, series of hydrocarbons and their derivatives, so the unsaturated compounds are the remaining series of open chain hydrocarbons and their unsaturated derivatives (p. 273).

HYDROCARBONS, ETHENE, OR OLEFIN SERIES.

The members of this series contain two atoms of carbon less than the corresponding terms of the methane series. They may be modified by addition, behaving as bivalent radicals, as well as by substitution. Their "Geneva" names terminate in **ene**.

Ethene—Ethylene—Olefiant gas—Olefin—Elayl—Heavy carburetted hydrogen— $\text{CH}_2:\text{CH}_2$ —is formed by the dry distillation of fats, resins, wood, and coal, and is a valuable constituent of illuminating gas.

It is formed synthetically: (1) By heating a mixture of alcohol, H_2SO_4 and sand. In this reaction ethyl-sulfuric acid is formed and decomposed: $\text{C}_2\text{H}_5.\text{HSO}_4 = \text{H}_2\text{SO}_4 + \text{CH}_2:\text{CH}_2$. (2) By the action of caustic potash upon ethyl bromid: $\text{CH}_3.\text{CH}_2\text{Br} + \text{KHO} = \text{KBr} + \text{H}_2\text{O} + \text{CH}_2:\text{CH}_2$. (3) By heating together acetylene and hydrogen, or by the action of nascent hydrogen upon copper acetylid: $\text{CH}:\text{CH} + \text{H}_2 = \text{CH}_2:\text{CH}_2$, or $\text{C}_2\text{Cu}_2 + 2\text{H}_2 = \text{CH}_2:\text{CH}_2 + 2\text{Cu}$. (4) By heating methylene iodid with copper: $2\text{CH}_2\text{I}_2 + 2\text{Cu} = \text{CH}_2:\text{CH}_2 + 2\text{CuI}_2$. (5) By the action of sodium or of zinc upon ethylene chlorid or bromid: $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl} + \text{Na}_2 = \text{CH}_2:\text{CH}_2 + 2\text{NaCl}$, or $\text{CH}_2\text{Br}.\text{CH}_2\text{Br} + \text{Zn} = \text{CH}_2:\text{CH}_2 + \text{ZnBr}_2$.

It is a colorless gas, tasteless, has a faint odor of salt water, sparingly soluble in water. Its critical temperature is 13° (55.4°F.); its critical pressure 60 atmospheres. It boils at -105° (-157°F.).

It burns with luminous flame, and forms explosive mixtures with air. By long contact with a red-hot surface it is decomposed into acetylene, methane, ethane, a tarry product, and carbon. It unites with hydrogen to form ethane, C_2H_6 ; with oxygen it unites explosively on approach of flame, to form carbon dioxid and water. It

combines with hydrobromic and hydriodic acids to form ethyl bromid, C_2H_5Br , and ethyl iodid, C_2H_5I . It combines with sulfuric acid to form ethyl-sulfuric acid: $CH_2:CH_2 + H_2SO_4 = C_2H_5.HSO_4$. Mixtures of ethene and chlorin explode, with copious deposition of carbon, on approach of flame. In diffuse daylight they unite slowly, with separation of an oily liquid, **ethylene chlorid**, or **dutch liquid**, $CH_2Cl.CH_2Cl$, to whose formation the name "olefiant gas" is due (p. 364). The same compound is formed when ethene is passed through a mixture of MnO_2 , $NaCl$, H_2SO_4 , and H_2O . When passed through alkaline solution of potassium permanganate, it is oxidized to oxalic acid and water: $2CH_2:CH_2 + 5O_2 = 2COOH.COOH + 2H_2O$; or, by careful oxidation by dilute solution of the same agent, it forms ethene glycol: $2CH_2:CH_2 + 2H_2O + O_2 = 2CH_2OH.CH_2OH$ (p. 295).

When inhaled, diluted with air, ethene produces effects somewhat similar to those of nitrous oxid.

Two groupings of $(C_2H_4)''$ are possible, $-CH_2.CH_2-$, and $CH_3.CH=$, the former produced by the breaking of the double bond between the carbon atoms in ethene, the latter by double substitution in ethane. Compounds containing the grouping $-CH_2.CH_2-$ are designated as **ethylene** or **ethene** compounds, e. g., **ethylene chlorid**, $ClCH_2.CH_2Cl$, b. p. 84° , those containing the grouping $CH_3.CH=$ are called **ethidene** or **ethylidene** compounds, e. g., **ethidene chlorid**, $CH_3.CHCl_2$, b. p. 58° .

Homologues of Ethene.—The superior homologues of ethene exist in coal gas and coal tar. They are formed by the methods 1 and 2, used for the preparation of ethene, but starting from the corresponding superior monoatomic alcohol. The lower terms are gaseous, the higher liquid at the ordinary temperature. They undergo reactions similar to those of ethene, and in addition, readily polymerize under the influence of sulfuric acid, zinc chlorid and other substances.

ETHINE, OR ACETYLENE SERIES.

Acetylene—*Ethine*— $HC \equiv CH$ —exists in coal gas, and is formed in the decomposition, by heat or otherwise, of many organic substances. It is formed: (1) By passing an electric arc in an atmosphere of hydrogen: $2C + H_2 = CH \equiv CH$. This is the only known synthesis of a hydrocarbon directly from the elements. (2) By the action of water upon calcium carbid: $C_2Ca + 2H_2O = HC \equiv CH + CaH_2O_2$. This method is used industrially for the preparation of acetylene for use as an illuminating gas. (3) By heating chloroform, bromoform or iodoform with sodium, copper, silver or zinc: $2CHCl_3 + 3Na_2 = 6NaCl + HC \equiv CH$. (4) By heating ethylene bromid with caustic potash. The reaction

occurs in two phases, vinyl bromid being formed as an intermediate product: $\text{CH}_2\text{Br}.\text{CH}_2\text{Br} + \text{KHO} = \text{CHBr}:\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$, and $\text{CHBr}:\text{CH}_2 + \text{KHO} = \text{CH}:\text{CH} + \text{KBr} + \text{H}_2\text{O}$.

Acetylene is a colorless gas, rather soluble in water, having a peculiar, disagreeable odor, that which is observed when a Bunsen burner burns within the tube. It is liquefied by a pressure of 48 atmospheres at 0° (32° F.). It forms explosive mixtures with air or oxygen. In contact with a red-hot surface, and in absence of air, it polymerizes to benzene $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$, an action which accounts for the presence of benzene in gas tar, and which is of great interest in connection with the relations between the open chain and the closed compounds (p. 433). Nascent hydrogen converts acetylene into ethene, C_2H_4 , and then into ethane, C_2H_6 . Under the influence of the electric discharge, it combines with nitrogen to form hydrocyanic acid: $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{CNH}$. It combines with HCl and with HI to form ethidene chlorid, $\text{CH}_3.\text{CHCl}_2$, or iodid, $\text{CH}_3.\text{CHI}_2$. Mixed with chlorin it detonates violently in diffuse daylight. The hydrogen atoms of acetylene may be replaced by metals to form **acetylids**, or **carbids**. Sodium and calcium acetylids are stable at high temperatures, but are decomposed by water with formation of acetylene. Silver and copper acetylids are highly explosive when dry, and explosions which have occurred when illuminating gas was in contact with brass or copper were probably due to the formation of the latter. The formation of copper acetylid, which separates as a blood-red precipitate when acetylene is conducted through a solution of cuprous chlorid, is utilized as a test for the presence of acetylene. Acetylene mercuric chlorid, $\text{C}_2(\text{HgCl})_2$, separates as a non-explosive, white precipitate when acetylene is passed through a solution of mercuric chlorid.

DIOLEFIN AND SUPERIOR SERIES.

The **diolefins** are isomeric with the hydrocarbons of the acetylene series, containing two double linkages, in place of one triple linkage. Thus **allene**, or **allylene**, $\text{CH}_2:\text{C}:\text{CH}_2$, is isomeric with **propene**, or **propylene**, $\text{CH}:\text{C}.\text{CH}_3$.

Trimethyl-ethylene—*Pentene*—*Amylene*—*Valerene*— $(\text{CH}_3)_2:\text{C}:-\text{CH}.\text{CH}_3$ —is a colorless, mobile liquid, boiling at 39° (102.2° F.), obtained by heating alcohol with a concentrated solution of zinc chlorid. It is used as an anæsthetic, and in the preparation of tertiary amyl alcohol (p. 294). Higher series, p. 273.

Olefin Terpenes—**Terpenogens**.—While most essential oils and other aromatic substances are closed chain compounds, some ethereal oils contain or yield unsaturated, open chain hydrocarbons, alcohols,

aldehydes or acids. Among the hydrocarbons are **myrcene**, and **anhydrogeraniol**, $C_{10}H_{16}$, the former obtained from bay-oil, the latter from oil of geranium. **Isoprene**, a product of distillation of caoutchouc, a liquid boiling at 37° (98.6° F.), is probably **methyl-divinyl**, $\begin{smallmatrix} CH_3 \\ \diagdown \\ CH_2 \end{smallmatrix} C.CH:CH_2$.

UNSATURATED HALOGEN DERIVATIVES.

These cannot be formed directly, because addition products, such as ethylene chlorid, are formed in preference: $CH_2:CH_2 + Cl_2 = CH_2Cl.CH_2Cl$. But, by indirect methods, halogen derivatives of both olefins and acetylenes have been obtained, such as **vinyl chlorid**, $CH_2:CHCl$, and **vinyl bromid**, $CH_2:CHBr$. The propylene derivatives are α $CH_3.CH:CHCl$, β $CH_3.CCl:CH_2$, or γ $CH_2Cl.CH:CH_2$, according to the position of the substitution.

The γ derivatives are the **allyl halids**, corresponding to allylic alcohol. **Allyl iodid**, $CH_2I.CH:CH_2$, and bromid are frequently used in syntheses. They are prepared by the action of hydriodic acid, or of iodine and phosphorus upon glycerol: $CH_2OH.CHOH.CH_2OH + 3HI = CH_2I.CH:CH_2 + 3H_2O + I_2$, and $CH_2OH.CHOH.CH_2OH + PBr_3 = CH_2Br.CH:CH_2 + H_3PO_3 + Br_2$.

Corresponding to allyl iodid, but referable to propylene, are **propargyl iodid** and **chlorid**, $CH:C.CH_2I$ and $CH:C.CH_2Cl$, the latter produced by the action of phosphorus trichlorid upon **propargyl alcohol** (p. 427).

UNSATURATED OXIDATION PRODUCTS OF UNSATURATED HYDROCARBONS

Like the paraffins, the olefins, acetylenes, diolefins, etc., yield alcohols, aldehydes, ketones, acids, oxids and esters (p. 282).

Vinyl Alcohol— $CH_2:CH.OH$ —the simplest of the **olefin alcohols**, is known only in a mercury compound. Although the radical, vinyl, $CH_2:CH$, is known in other compounds (see Neurin, p. 384), there is atomic transposition, with formation of aldehyde, CH_3CHO , under conditions in which vinyl alcohol might be formed.

Allyl Alcohol— $CH_2:CH.CH_2OH$ —is formed: (1) By the action of sodium upon dichlorhydrin: $CH_2Cl.CHCl.CH_2OH + Na_2 = CH_2:CH.CH_2OH + 2NaCl$; (2) by heating allyl iodid with water: $CH_2:CH.CH_2I + H_2O = CH_2:CH.CH_2OH + HI$; (3) by reduction of acrolein by nascent hydrogen: $CH_2:CH.CHO + H_2 = CH_2:CH.CH_2OH$; (4) by heating glycerol with formic acid, which first forms a glycerol ester, which then splits to allylic alcohol, carbon dioxid and water: $CH_2OH.CHOH.CH_2(OOC.H) = CH_2OH.CH:CH_2 + CO_2 + H_2O$. Oxalic acid, which yields formic acid, may be used in place of the latter.

It is a colorless, mobile liquid, solidifies at -50° (-58° F.), boils at 97° (206.6° F.), sp. gr. 0.8507 at 25° (77° F.), soluble in water, has an odor resembling the combined odors of alcohol and essence of mustard, burns with a luminous flame. It is isomeric with propylic aldehyde and with acetone. Oxidizing agents, such as silver oxid, convert it first into the corresponding aldehyde, **acrolein**, then into the acid, **acrylic acid**. It does not unite readily with hydrogen, but, in presence of nascent H, union takes place slowly, with formation of normal propyl alcohol. It forms products of addition with chlorine, bromine and iodine, similar to those derived from glycerol. Substitution compounds have also been obtained, such as α bromallyl alcohol, $\text{CH}_2:\text{CBr}.\text{CH}_2\text{OH}$, derived from β dibromo-propylene, $\text{CH}_2:\text{CBr}.\text{CH}_2\text{Br}$.

Propargyl Alcohol— $\text{CH}:\text{C}.\text{CH}_2\text{OH}$ —first of the **acetylene alcohols**, is formed by the action of caustic potash upon α bromallyl alcohol: $\text{CH}_2:\text{CBr}.\text{CH}_2\text{OH} + \text{KHO} = \text{CH}:\text{C}.\text{CH}_2\text{OH} + \text{KBr} + \text{H}_2\text{O}$.

Rhodinol— $\text{C}_{10}\text{H}_{20}\text{O}$ —b. p. 114° ; **geraniol**, $\text{C}_{10}\text{H}_{18}\text{O}$, b. p. 120° ; and **linalool**, $\text{C}_{10}\text{H}_{18}\text{O}$, b. p. 198° are **diolefin alcohols**, which are the chief constituents of the essential oils of rose, geranium, pelargonium, lavender, bergamot, etc.

Acrylic Aldehyde—**Acrolein**— $\text{CH}_2:\text{CH}.\text{CHO}$ —the first of the series of **olefin aldehydes**, is the substance which causes the disagreeable odor developed when fats or oils are overheated. It is formed: (1) By oxidation of allylic alcohol; (2) by distilling glycerol with strong H_2SO_4 or with KHSO_4 : $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH} = \text{CH}_2:\text{CH}.\text{CHO} + 2\text{H}_2\text{O}$.

Acrolein is a colorless liquid, having a pungent odor, and giving off a vapor which is intensely irritating; sp. gr. 0.841 at 20° (68° F.), boils at 52° (125.6° F.), soluble in 2-3 parts of water. Oxidizing agents convert it into acrylic acid. Nascent hydrogen reduces it to allyl alcohol. It does not combine with alkaline bisulfites. It reduces ammoniacal silver nitrate solution as does acetic aldehyde. It suffers change even when kept in closed vessels, and deposits a white, flocculent material, which is called **disacryl**, while formic, acetic and acrylic acids are also produced.

Croton Aldehyde— $\text{CH}_3.\text{CH}:\text{CH}.\text{CHO}$.—By the action of diffuse daylight upon a mixture of acetic aldehyde, H_2O and HCl , an oily liquid is slowly formed, which consists chiefly of **aldol**, or β **oxybutyraldehyde**, $\text{CH}_3.\text{CHOH}.\text{CH}_2.\text{CHO}$. This, when heated, is decomposed into croton aldehyde and water: $\text{CH}_3.\text{CHOH}.\text{CH}_2.\text{CHO} = \text{CH}_3.\text{CH}:\text{CH}.\text{CHO} + \text{H}_2\text{O}$.

Croton aldehyde is a colorless liquid; boils at 105° (221° F.), gives off highly irritating vapors; sp. gr. 1.033 at 0° (32° F.). It is reduced by nascent H to **crotonyl alcohol**, $\text{CH}_3.\text{CH}:\text{CH}.\text{CH}_2\text{OH}$.

Propargyl Aldehyde— $\text{CH}:\text{C}.\text{CHO}$ —is an acetylene aldehyde, a liquid, which boils at 59° (138.2° F.).

Citronellal, $\text{C}_{10}\text{H}_{18}\text{O}$, b. p. 104° , is an olefin aldehyde, existing in citronella and other essential oils. **Geranial**, $\text{C}_{10}\text{H}_{16}\text{O}$, b. p. 226° , is a diolefin aldehyde existing in lemon oil, and formed from geraniol.

Mesityl Oxid, $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CO}.\text{CH}_3$, and **Phorone**, $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CO}.\text{CH}:\text{C}(\text{CH}_3)_2$, are examples, respectively, of olefin and diolefin ketones. They are produced together by the action of dehydrating agents, such as H_2SO_4 and ZnCl_2 , upon acetone. Mesityl oxid is a liquid, boiling at 130° , and having the odor of peppermint. Phorone is a solid, fusing at 28° , and boiling at 196° . **Methylheptenone**, $(\text{CH}_3)_2\text{C}:\text{CH}.\text{CH}_2.\text{CH}_2.\text{CO}.\text{CH}_3$, another olefin ketone, is a liquid having a penetrating odor, boiling at 173° , which exists in, or is produced from, many essential oils.

Oleic Acids.—The acids of this series are monocarboxylic acids derived from the olefins, and contain two atoms of hydrogen less than the corresponding terms of the acetic series. They are formed: (1) By oxidation of their corresponding alcohols or aldehydes. Thus allylic alcohol, $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$, or acrolein, $\text{CH}_2:\text{CH}.\text{CHO}$, yield acrylic acid, $\text{CH}_2:\text{CH}.\text{COOH}$; (2) by the action of alcoholic KHO upon the monohalogen fatty acids. Thus β monobromo propionic acid yields acrylic acid: $\text{CH}_2\text{Br}.\text{CH}_2.\text{COOH} + \text{KHO} = \text{CH}_2:\text{CH}.\text{COOH} + \text{KBr} + \text{H}_2\text{O}$; (3) by dehydration of acids of the oxyacetic series. Thus ethylene lactic acid (β oxypropionic, p. 342) forms acrylic acid when heated: $\text{CH}_2\text{OH}.\text{CH}_2.\text{COOH} = \text{CH}_2:\text{CH}.\text{COOH} + \text{H}_2\text{O}$; (4) from the allyl halids (p. 426), by conversion into cyanids and saponification. Thus crotonic acid is obtained from allyl iodid: $\text{CH}_2:\text{CH}.\text{CH}_2\text{I} + \text{KCN} = \text{CH}_2:\text{CH}.\text{CH}_2\text{CN} + \text{KI}$, and $\text{CH}_2:\text{CH}.\text{CH}_2\text{CN} + 2\text{H}_2\text{O} + \text{HCl} = \text{CH}_2:\text{CH}.\text{CH}_2.\text{COOH} + \text{NH}_4\text{Cl}$ (p. 328).

The oleic acids combine with the hydracids to form monohalogen fatty acids, the halogen assuming the position furthest removed from the carboxyl. Thus acrylic acid and hydriodic acid form β iodo propionic acid: $\text{CH}_2:\text{CH}.\text{COOH} + \text{HI} = \text{CH}_2\text{I}.\text{CH}_2.\text{COOH}$. Heated with caustic alkalies to 100° , they form oxyacids. Thus acrylic acid forms α lactic acid: $\text{CH}_2:\text{CH}.\text{COOH} + \text{KHO} = \text{CH}_3.\text{CHOH}.\text{COOK}$. But, when fused with caustic alkalies, they are decomposed into fatty acids, with loss of H. Thus acrylic acid yields formic and acetic acids: $\text{CH}_2:\text{CH}.\text{COOH} + 2\text{KHO} = \text{H}.\text{COOK} + \text{CH}_3.\text{COOK} + \text{H}_2$. The $\beta\gamma$ acids, i. e., those in which the double bond is between the β and γ positions, as in ethidene propionic acid, $\text{CH}_3.\text{CH}:\text{CH}.\text{CH}_2.\text{COOH}$, when heated with H_2SO_4 form lactones (p. 368).

Acrylic Acid— $\text{CH}_2:\text{CH}.\text{COOH}$ —is best obtained by oxidizing acrolein with silver oxid. It is a liquid below 7° (44.6° F.), boils

at 140° (284° F.), mixes with water, and has an odor like that of acetic acid.

Crotonic Acids.—Three crotonic acids are known, two of which are space isomerids (pp. 311, 430): **Ordinary crotonic acid**,

$\text{CH}_3 \text{---} \text{C} \text{---} \text{C} \begin{matrix} \text{COOH} \\ \text{H} \end{matrix}$, a crystalline solid, fusible at 72° (161.6° F.);

isocrotonic acid, $\text{H} \text{---} \text{C} \text{---} \text{C} \begin{matrix} \text{COOH} \\ \text{CH}_3 \end{matrix}$, a liquid boiling at 75° (167° F.),

and **methacrylic acid**, $\text{CH}_2 \text{---} \text{C} \begin{matrix} \text{COOH} \\ \text{CH}_3 \end{matrix}$, a crystalline solid, f. p. 16°, b. p. 160°.

Angelic Acid— $\text{H} \text{---} \text{C} \begin{matrix} \text{COOH} \\ \text{CH}_3 \end{matrix}$ —is a crystalline solid, f. p. 45°, b. p. 185°, having an aromatic odor, soluble in water, alcohol and ether. It exists free in angelica root, and, in its esters, in oil of cumín and in oil of anthemis. **Tiglic acid**—**Methyl-crotonic acid**— $\text{CH}_3 \text{---} \text{CH} \text{---} \text{C} \begin{matrix} \text{COOH} \\ \text{CH}_3 \end{matrix}$ —isomeric with angelic acid, exists as a glycerid in croton oil, and, as its amyl ester, in oil of cumín. It is a crystalline solid, f. p. 65°, b. p. 198°.

Hypogæic Acid— $\text{C}_{15}\text{H}_{29} \text{---} \text{COOH}$ —accompanies arachic acid (p. 334) as its glycerid, in peanut oil. It is a crystalline solid, f. p. 33°, b. p. 236°.

Oleic Acid— $\text{CH}_3 \text{---} (\text{CH}_2)_7 \text{---} \text{CH} \text{---} \text{CH} \text{---} (\text{CH}_2)_7 \text{---} \text{COOH}$ —exists as its glyceric ester in fats and fixed oils, and is obtained in an impure form, on a large scale, as a by-product in the manufacture of stearin candles.

Pure oleic acid is a white, pearly, crystalline solid, fuses at 14° (57.2° F.), odorless, tasteless, soluble in alcohol and in ether, insoluble in water, sp. gr. 0.808 at 19° (66.2° F.), and neutral in reaction. Exposed to air, the liquid acid absorbs oxygen, and becomes yellow, rancid in taste and odor, acid in reaction, and incapable of solidification on cooling. Nitric acid oxidizes it, with formation of the lower fatty acids and **sebacic acid**, $\text{C}_{10}\text{H}_{18}\text{O}_4$. Heated to 200° (392° F.) with excess of caustic potash, it is split into palmitic and acetic acids: $\text{C}_{18}\text{H}_{34}\text{O}_2 + 2\text{KHO} = \text{C}_{16}\text{H}_{31}\text{O}_2\text{K} + \text{C}_2\text{H}_3\text{O}_2\text{K} + \text{H}_2$. The oleates of the alkaline metals are soft, soluble soaps; those of the earthy metals are insoluble in water. The action of iodine and of bromine upon oleic acid is utilized in the analysis of fats and oils. At the ordinary temperature the fatty acids, including palmitic and stearic, are not affected by iodine, but the double bond in oleic acid is broken, and one molecule of oleic acid combines with two atoms of iodine. Under like conditions each molecule of linoleic acid (see below) takes up four atoms of iodine. The amount of iodine which a given weight of a fat or oil can combine with will increase with its tenure of oleic, or, particularly, of linoleic acid. "Hubl's **iodine**

number" of a fat or oil is the quantity of iodine which 100 grams of the substance can take up under the conditions of the process, and is an important factor for its identification.

Elaidic Acid— $C_{17}H_{33}.COOH$ —is an isomere of oleic acid, produced from it by the action of nitrous acid. It is a crystalline solid, fusible at 51° (123.8° F.). Its formation is utilized to distinguish non-drying from drying oils (p. 366). The former, containing oleic acid, solidify when acted on by nitrous acid; the latter, containing linoleic acid, do not.

Ricinoleic Acid— $CH_3.(CH_2)_5.CHOH.CH_2.CH:CH.(CH_2)_7.COOH$ —is an unsaturated oxyacid, which exists as its glyceric ester in castor oil.

Linoleic Acid— $C_{17}H_{31}.COOH$ —is an unsaturated, pure acid, containing two atoms of hydrogen less than oleic acid. It exists as its glyceric ester in the drying oils, which dry and solidify on exposure to air.

Propargylic Acid—*Propiolic Acid*— $CH:C.COOH$ —corresponding to propargylic alcohol, is an example of an **acetylene monocarboxylic acid**. It is a liquid, having the odor of acetic acid. **Sorbic acid**, $CH_3.CH:CH.CH:CH.COOH$, is a **diolefin monocarboxylic acid**, derived from **parasorbic acid**, which is an unsaturated **oxyolefin acid** occurring in the berries of the mountain ash.

Olefin dicarboxylic Acids.—The acids of this series contain two atoms of hydrogen less than the corresponding acids of the oxalic series, and they consequently bear the same relation to those acids that the acids of the oleic series bear to those of the acetic series.

Esters of three acids having the composition $C_2H_2(COOH)_2$ are known. The free acid corresponding to one of these, **methylenemalonic ester**, $CH_2:C\begin{matrix} \swarrow COO(C_2H_5) \\ \searrow COO(C_2H_5) \end{matrix}$, is not known. The other two, **fumaric** and **maleic acids**, are "space isomerids" (p. 314). **Fumaric acid** is considered to have the axial symmetric structure:

$\begin{matrix} H.C.COOH \\ || \\ HOOC.C.H \end{matrix}$, because it does not yield an anhydride, and because, on oxidation, it yields racemic acid, while **maleic acid** has the plane symmetrical structure, because, owing to the closer proximity of the car-

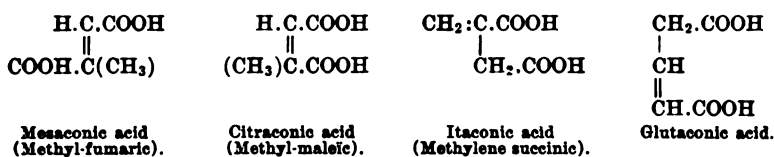
$\begin{matrix} H.C.COOH \\ || \\ H.C.COOH \end{matrix}$ boxyls, $\begin{matrix} H.C.CO \\ || \\ H.C.CO \end{matrix}$, it readily forms an anhydride, $\begin{matrix} H.C.CO \\ || \\ H.C.CO \end{matrix} > O$, and because on oxidation it yields inactive, or meso-tartaric acid (see p. 313 and Fig. 40, *ibid.*).

Fumaric acid exists free in many plants, notably in Iceland moss. Fumaric and maleic acids are readily converted one into the other by simple heating, and the two are produced together by the action of

heat upon malic acid (p. 344), or by boiling solutions of monobromo-succinic acid (p. 337).

Fumaric acid crystallizes in small prisms, almost insoluble in cold water, which sublime at 200° (392° F.). Maleic acid fuses at 130° (266° F.), and boils at 160° (320° F.). Both fumaric and maleic acids are converted into succinic acid by nascent hydrogen.

Five unsaturated, open chain acids are known having the formula $C_3H_4(COOH)_2$, the next superior homologues of fumaric and maleic acids. One of these, **ethidene malonic acid**, is only known in its esters $CH_3.CH:C\begin{smallmatrix} \diagup COO(C_2H_5) \\ \diagdown COO(C_2H_5) \end{smallmatrix}$. The structural formulæ of the others are:



Mesaconic acid is formed by heating citraconic or itaconic acid with water at 200° (392° F.). It is difficultly soluble in water, and fuses at 202° (395.6° F.). **Citraconic acid** is obtained from its anhydrid, $\begin{array}{c} H.C.CO \\ || \\ CH_3.C.CO \end{array} \rangle O$, formed in the distillation of citric acid, by heating with water. Easily soluble in water, f. p. 80° (176° F.). **Itaconic acid** is similarly obtained from its anhydrid, a product of distillation of aconitic acid, f. p. 161° (320.2° F.). **Glutaconic acid** is formed by the action of barium hydroxid upon coumalic acid, an α -pyrone monocarboxylic acid (p. 517): $OC\begin{array}{c} \diagup O \\ \diagdown CH:CH \end{array} \rangle C.COOH$. It fuses at 132° (269.6° F.).

Aconitic Acid— $COOH.CH_2.C(COOH):CH.COOH$ —is an **olefin tricarboxylic acid**. It exists as its Ca salt in a number of plants, including aconitum, equisetum, sugar-cane and beet-root. It is formed by heating citric acid (p. 346), either alone or with HCl or H_2SO_4 . It is also obtained synthetically from a mixture of acetic and oxalic esters. It forms crystalline plates or prisms, soluble in water, alcohol, and ether, fuses at 191° (375.8° F.). Heat decomposes it into itaconic acid and CO_2 . Nascent hydrogen reduces it to tricarballic acid (p. 338).

Allyl Oxid—*Allylic ether*— $(CH_2:CH.CH_2)_2O$ —is an example of the unsaturated ethers. It exists in small quantity in crude essence of garlic, and is formed by the action of allyl iodid upon sodium-allyl oxid. It is a colorless liquid, having the odor of garlic, insoluble in water, boiling at 82° (179.6° F.). Mixed ethers are also known, such as propargyl ethyl ether, $CH:C.CH_2.O.CH_2.CH_3$.

UNSATURATED SULFUR AND NITROGEN COMPOUNDS.

Allyl Sulfid— $(\text{CH}_2:\text{CH}.\text{CH}_2)_2\text{S}$ —corresponding to the oxid, is the principal constituent of volatile oil of garlic, obtained by distilling garlic with water. It is formed by the action of alcoholic solution of potassium sulfid upon allyl iodid. It is a colorless oil, lighter than water, soluble in alcohol and in ether, boils at 140° (280° F.).

Allyl Isothiocyanate—*Mustard oil*— $\text{S}:\text{C}:\text{N}.\text{CH}_2.\text{CH}:\text{CH}_2$ —is the chief constituent of volatile oil of mustard, and of radish oil. It is prepared artificially by distilling allyl bromid or iodid with potassium or silver thiocyanate: $\text{S}:\text{C}:\text{N}.\text{Ag} + \text{CH}_2\text{I}.\text{CH}:\text{CH}_2 = \text{S}:\text{C}:\text{N}.\text{CH}_2.\text{CH}:\text{CH}_2 + \text{AgI}$. It does not exist preformed in the mustard seeds, but is produced by the decomposition of a glucosid, **potassium myronate** (p. 467), in the presence of water under the influence of an enzym, also contained in the seeds, called **myrosin**. The action takes place at 0° (32° F.), but not at temperatures above 40° (104° F.). The activity of myrosin is also impaired by the presence of acetic acid (vinegar). The pungent, rubefacient and vesicant actions of mustard are due to mustard oil.

Pure allyl isothiocyanate is a colorless oil, sp. gr., 1.015 at 20° (68° F.), boils at 150° (302° F.), has a penetrating, pungent odor, sparingly soluble in water, very soluble in alcohol and in ether. Exposed to air it gradually turns brownish-yellow, and deposits a resinoid material. Heated with HCl or with H_2O , it is decomposed into carbon dioxid, hydrogen sulfid and **allyl-amin**: $\text{S}:\text{C}:\text{N}.\text{CH}_2.\text{CH}:\text{CH}_2 + 2\text{H}_2\text{O} = \text{CO}_2 + \text{SH}_2 + \text{NH}_2.\text{CH}_2.\text{CH}:\text{CH}_2$.

Allyl-amin is the superior homologue of **vinyl-amin**, which is capable of uniting with sulfur dioxid and water to produce taurin or amido-isethionic acid (p. 421): $\text{NH}_2.\text{CH}:\text{CH}_2 + \text{SO}_2 + \text{H}_2\text{O} = \text{NH}_2.\text{CH}_2.\text{CH}_2.\text{SO}_3\text{H}$.

CLOSED CHAIN COMPOUNDS—CYCLIC COMPOUNDS.

These compounds, which include many important natural products, and a practically unlimited number of synthetic compounds, differ from the members of the open chain series in that they contain a group of more than two atoms united together by exchange of valences in such a manner* as to form a **closed chain**, or **ring**, or **nucleus**. If all the atoms so united are carbon atoms the substance belongs to the **carbocyclic** class; if an element other than carbon enters into the formation of the ring the substance is **heterocyclic**.

Some closed chain compounds are produced by the interaction of two open chain compounds, as in the formation of certain diamins (p. 385) and compound ureas (p. 406). Others, such as the lactids (p. 368), lactones (pp. 368, 412), and lactams (p. 413), are produced by internal reaction in an open chain molecule. But the principal method of formation of closed chain compounds is by polymerization. In some cases this takes place at comparatively low temperatures, as in the formation of trioxymethylene from formaldehyde (p. 301), and of the polymeric thioaldehydes and their sulfones (p. 373).

Among the instances of formation of cyclic from acyclic compounds there is one of polymerization at a high temperature which is of special interest as bearing upon the constitution of the cyclic compounds. The central figure of the carbocyclic compounds is **benzene**, C_6H_6 , which is obtained principally from gas-tar. Coal gas contains **acetylene**, C_2H_2 , and it is easy to conceive that one or two of the bonds uniting the two carbon atoms in acetylene may be loosened under the influence of heat, and that a molecule of benzene may be produced by fusion of three molecules of acetylene: $3C_2H_2 = C_6H_6$. The product so obtained is neither dipropargyl, $HC:C.CH_2-CH_2.C:CH$, nor dimethyl diacetylene, $H_3C.C:C.C:C.CH_3$ (p. 273), but another substance, the nature of whose substituted derivatives indicates that the six hydrogen atoms are of equal value, and therefore similarly attached to carbon atoms; and, there being three bisubstituted derivatives (p. 436), to at least three different carbon atoms. These conditions can only be fulfilled by a cyclic structure of the molecule of benzene and its derivatives (p. 435). Pyridin also, which has a prominence among the heterocyclic compounds corresponding to that of benzene among the carbocyclic, has been obtained from acetylene and hydrocyanic acid by a fusion very similar to that by which acetylene alone forms benzene: $2C_2H_2 + HCN = C_5H_5N$. It is also formed by the action of heat upon substances containing nitrogen as well as carbon (p. 517)

CARBOCYCLIC COMPOUNDS.

Carbocyclic compounds are known containing from three to seven carbon atoms in a ring. Compounds are also known containing a much larger number of carbon atoms, but these are formed by fusion or union of two or more rings of six carbon atoms or less, or by the attachment of an open chain grouping upon a closed chain one (p. 439). The hexacarbo-cyclic compounds are far more numerous and important than the others.

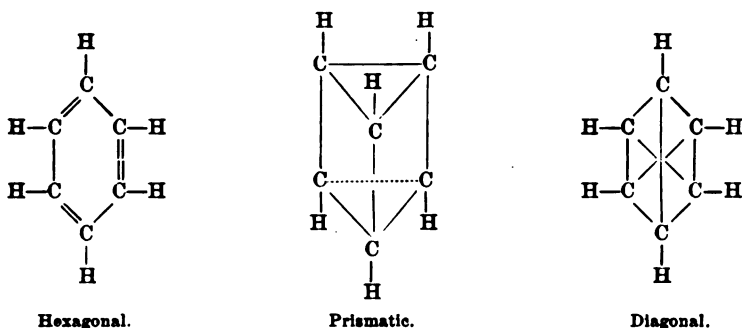
The mononuclear carbocyclic hydrocarbons have algebraic formulæ varying from C_nH_{2n} to C_nH_{2n-6} , and are isomeric with the unsaturated open chain hydrocarbons (p. 273). Those of the series C_nH_{2n} are known as **polymethylenes**, being considered as formed by the union of a number of methylene groups, CH_2 . Thus **hexahydrobenzene** is **hexamethylene**, $CH_2 \begin{smallmatrix} CH_2.CH_2 \\ CH_2.CH_2 \end{smallmatrix} CH_2$. But the chemical relations of the polymethylenes to the saturated hydrocarbons is closer than that to their isomeres, the olefins, because, containing no double linkages, they cannot be modified by addition without disruption of the ring. So long as the cyclic formation is maintained, the polymethylenes are saturated compounds, as are the paraffins. For this reason their "Geneva" names are the same as those of the paraffins of like carbon content, to which is prefixed the syllable "**cyclo**," and they are known generically as **cycloparaffins**; or the symbol **R** is used in place of the syllable "cyclo." The hydrocarbons of the series C_nH_{2n-2} , isomeric with the acetylenes and diolefins, are referable to the latter, not to the former, as they cannot contain a triple linkage in the ring. But, containing only one double linkage, they are more closely related to the olefins. Therefore **tetrahydrobenzene**, $CH \begin{smallmatrix} CH.CH_2 \\ CH_2.CH_2 \end{smallmatrix} CH_2$, isomeric with hexadiène, $CH_2:CH.CH_2.CH_2.CH_2:CH_2$, containing but one double linkage, is **cyclo-hexene**, or **R-hexene**. Similarly **dihydrobenzene**, $CH \begin{smallmatrix} CH_2.CH_2 \\ CH.CH \end{smallmatrix} CH$, is a **cyclo-diolefin**: **R-hexadiène**; and **benzene** a **cyclotriolefin**: **R-hexatriène**.

The cycloparaffins are formed by the action of sodium upon the dibromoparaffins. Thus trimethylene is obtained from trimethylene bromid: $CH_2Br.CH_2.CH_2Br + Na_2 = CH_2 \begin{smallmatrix} CH_2 \\ | \\ CH_2 \end{smallmatrix} + 2NaBr$.

Tri-, tetra-, penta-, and hepta-carbocyclic hydrocarbons, and their numerous derivatives, notably acids and ketones, are known. They are not as yet, however, of medical interest, except that certain tetra-, and penta-compounds are among the decomposition products of certain alkaloids.

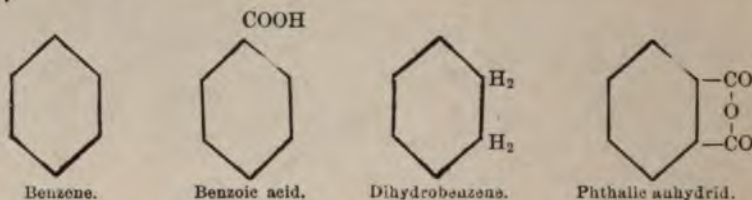
HEXACARBOCYCLIC COMPOUNDS — AROMATIC SUBSTANCES.

These compounds, which are very numerous and important, all contain a group of six carbon atoms, to which are attached six, eight, ten or twelve univalents, or their equivalent. As the simplest representative of the class is benzene, C_6H_6 , and as all of these bodies may be derived from benzene, directly or indirectly, and yield that hydrocarbon on decomposition, *the aromatic substances may be considered as derivatives of benzene*. This being the case, the constitution of benzene itself is of great importance, and has been the subject of much study. Several schematic representations of the structure of the benzene molecule have been suggested, the most demonstrative of which are the hexagonal form of Kekulé, the prismatic form of Ladenburg, and the diagonal form of Claus:



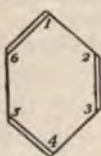
In the hexagonal formula the carbon atoms exchange one and two valences alternately, each being attached to two others; in the prismatic form each carbon atom is attached to three others by single valences; and in the diagonal form the hexagon is retained, but, in place of double linkages, a central linkage between all the carbon atoms is substituted. All of these formulæ represent the equivalence of the carbon atoms, and the constitution of isomeres equally well (see below). The prismatic formula cannot be modified to represent a constitution of the additive derivatives of benzene, such as dihydrobenzene, $CH\langle\begin{smallmatrix} CH_2.CH_2 \\ CH.CH \end{smallmatrix}\rangle CH$, and tetrahydrobenzene, $CH\langle\begin{smallmatrix} CH_2.CH_2 \\ CH.CH_2 \end{smallmatrix}\rangle CH_2$. Neither the prismatic nor the diagonal formula admits double linkages between carbon atoms in the ring. That these exist is shown, however, by the formation of the additive products mentioned, by the formation of anhydrides from ortho-derivatives only (see below), and by certain physical properties. Moreover, the hexagonal formula ac-

cords well with the tetrahedral representation of the valences of the carbon atom (p. 312), the six tetrahedra being alternately united by edges and apexes in benzene, and by apexes in hexahydrobenzene. For these (and other) reasons, chemists have very generally adopted the hexagonal expression, although it still leaves something to be desired. The figure of a hexagon is used in chemical writings to represent the benzene ring. If used alone it represents a molecule of benzene, C_6H_6 ; and to represent the products of substitution the symbols of the substituted group are written in the proper position, thus :



Isomery of Benzene Substitution Products.—(1) *The six atoms of hydrogen in benzene are of equal value.* There exists but one mono-substituted derivative of benzene containing any given univalent: one chlorobenzene, C_6H_5Cl , one nitro-benzene, $C_6H_5(NO_2)$, one amido-benzene, $C_6H_5(NH_2)$, one benzoic acid, $C_6H_5.COOH$, etc. Therefore, benzene is symmetrical in structure, and its hydrogen atoms equal each other in value, as do those of methane, while those of pyridin (p. 509) are not all of like value.

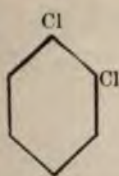
2. *Any hydrogen atom selected in the benzene ring is symmetrically placed in reference to two pairs of hydrogen atoms, and to the sixth hydrogen atom individually.* With all di-, tri-, and tetra-substituted derivatives of benzene, containing like substituted univalents, there are three isomeres. Three dichloro-, three trichloro-, and three tetrachloro-benzenes, etc., and in no instance are more than three known. There is but one explanation of the facts mentioned above, namely, that the different bi-, tri-, and tetra-derivatives are produced by differences in the relative positions of the substituted groups, by differences in "orientation," as among the aliphatic compounds, the several oxyacids are "place isomeres" of each other (p. 339).



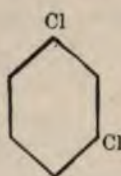
The hexagonal formula of benzene is very convenient for showing the structure of the several isomeres. For this purpose the carbon atoms are numbered, beginning, for convenience, at the top and proceeding clockwise.

It has been demonstrated that in some of the bisubstituted derivatives the two substituted groups are attached to adjacent carbon atoms, i. e., to 1-2, 2-3, 3-4, 4-5, 5-6, or 6-1.

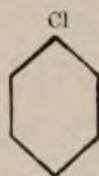
Clearly for each carbon atom there is a pair of adjacent positions, as 1-2 and 1-6, 2-1 and 2-3, etc., which are equivalent to each other.* In other bisubstituted derivatives it may be shown that the two substituted groups are attached to carbon atoms, separated from each other by one carbon atom on one side and by three on the other, an arrangement which renders the hexagon **unsymmetrical**. Such positions are 1-3, 2-4, 3-5, 4-6, 5-1, and 6-2. Or, for each carbon atom there is a pair of equivalent unsymmetrical positions, as 1-3 and 1-5, etc. There remains but one other arrangement possible, the **symmetrical**, or diagonal, 1-4, 2-5, 3-6. With the tri- and tetra-substituted derivatives there are also three possible arrangements: the **adjacent**, **vicinal**, or **consecutive**, as 1-2-3, 2-3-4; 1-2-3-4, or 2-3-4-5; the **unsymmetrical**, as 1-2-4, 3-4-6; 1-2-3-5, or 3-4-5-1; and the **symmetrical**, as 1-3-5, 2-4-6; 1-2-4-5, or 3-4-6-1. Compounds in which the substitution is adjacent are designated as **ortho-compounds** (*ὀρθός*=straight), or, in writing, by the abbreviation o-, or by the figures 1-2, etc. Thus $C_6H_4(OH)_{2(1-2)}$, o-diphenol. Unsymmetrical compounds are designated as **meta-compounds** (*μετά*=after), or, abbreviated, m-, or by the figures, 1-3, etc.: e. g., $C_6H_3(Br)_{3(1-2-4)}$, m-tribromobenzene. Symmetrical compounds are designated as **para-compounds** (*παρά*=beside), abbreviated p-, or 1-4, etc.: e. g., $C_6H_2(NH_2)_{4(1-2-4-5)}$, p-tetraamido-benzene. Or, to illustrate by the formulæ of the di- and tetra-chlorobenzenes:



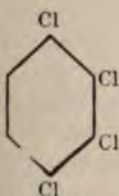
1-2



1-3

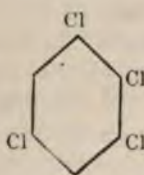


1-4



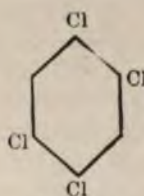
1-2-3-4

Adjacent.
Ortho.



1-2-3-5

Unsymmetrical.
Meta.

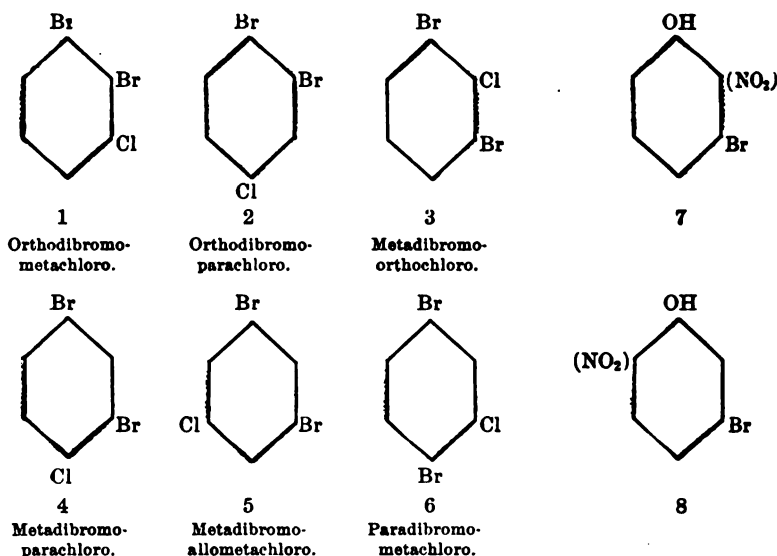


1-2-4-5

Symmetrical.
Para.

*NOTE.—The principal objection to the hexagonal formula of benzene (and stated by Kekulé himself) is that these two positions are not entirely equivalent, as in the position 1-2 the grouping is $=C-C=$, while in 1-6 it is $=C=C-$, and that consequently there should be two ortho derivatives, while but one is known. The student is referred to more extended works for a discussion of this subject.

In the bisubstituted derivatives it is immaterial whether the two substituted groups are of the same kind or different. But when, in a trisubstituted derivative, the substituted groups are not the same in kind, the number of possible isomeres is increased. Thus there are six possible chloro-dibromobenzenes (formulae 1 to 6 below), of which two (1 and 2) are derived from orthodibromobenzene, $C_6H_4:Br_2$, three (3, 4, and 5) from metadibromobenzene, $C_6H_4:Br_2$, and one (6) from paradibromobenzene, $C_6H_4:Br_2$. The number of possible trisubstituted derivatives is increased to ten when all three substituted groups are of different kind.



In naming these derivatives, the characterizing group of the parent substance is given the position 1 in the hexagon, the prefix "ortho" is applied to the name of the group occupying one of the ortho positions 2 and 6, "meta" to that occupying one of the meta positions 3 and 5, and "para" to that occupying the para position 4. Thus the substance having the formula 7 above is **orthonitro-meta-bromo-phenol**. But another substance is known, not identical with this, having the formula 8 above, in which the nitro group occupies the second ortho position, 6. To distinguish substances such as these, the designation "allortho" is given to the position 6, and the designation "allometa" to the position 5. Thus the substance having the formula 8 is **metabromo-allorthonitro-phenol**. When formulae are used the numerals corresponding to the position of substitution, enclosed in brackets, are placed after the symbols. Thus 7 is written: $C_6H_3(OH)(NO_2)_{[2]}Br_{[3]}$, and 8: $C_6H_3(OH)Br_{[3]}(NO_2)_{[6]}$.

Classification of Aromatic Substances.—The benzene derivatives may be classified into five classes :

A. Compounds containing a single benzene nucleus, unmodified except by substitution for hydrogen. Monobenzenic compounds. Includes benzene and its homologues, and the phenols, alcohols, acids, etc., derived from them.

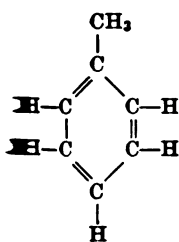
B. Compounds containing a single benzene nucleus in which one (or more) of the double bonds has been converted into a single one, thus adding two, four, or six valences to the carbon ring. Monohydrobenzenic compounds. Includes the cyclohexadiènes, cyclohexenes, and cyclohexanes (p. 434), and their derivatives, among which are the terpenes and camphors.

C. Compounds containing two (or more) benzene nuclei, or benzene and pentacarbocyclic rings, fused together, and having two carbon atoms in common. Includes indene, fluorene, naphthalene, anthracene, and phenanthrene and their derivatives. Compounds with condensed nuclei.

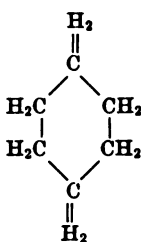
D. Compounds containing two (or more) benzene rings, directly united by loss of two H atoms. Diphenyl and its derivatives.

E. Compounds containing two (or more) benzene nuclei, united by aliphatic groups. Includes di- and polyphenyl paraffins, olefins and acetylenes and their derivatives.

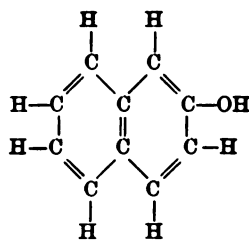
The following formulæ will serve to indicate the differences in constitution of the several classes :



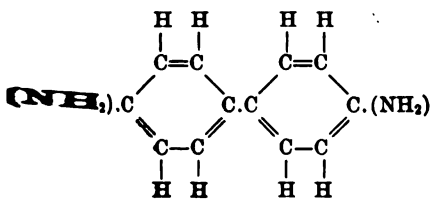
(A)
Methyl-benzene.



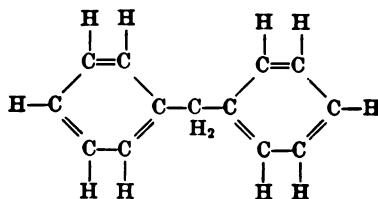
(B)
Hexahydrobenzene.



(C)
 β Naphthol.



(D)
p, p'-Diamido-diphenyl.



(E)
Diphenyl-methane.

A. MONOBENZENIC COMPOUNDS.

HYDROCARBONS.

Benzene — *Benzol* — C_6H_6 — (not to be confounded with *benzine*, a mixture of hydrocarbons of the series C_nH_{2n+2} , obtained from petroleum — p. 276) does not exist in nature. It is obtained, pure, by decomposing benzoic acid by heating with slaked lime: $C_6H_5\cdot COOH + CaH_2O_2 = CaCO_3 + C_6H_6 + H_2O$. It is produced in the distillation of coal, and exists in coal tar, from which it is obtained for use in the arts.

Coal tar, or gas tar, is a very complex mixture, containing forty or fifty substances — hydrocarbons, phenols and bases — and is the crude material from which many important substances are obtained. In working it, it is first distilled, four fractions being collected: (1) *Light oil*, distilling below 150° (302° F.); (2) *carbolic oil*, or *middle oil*, distilling below 230° (446° F.). Contains phenols and naphthalene. (3) *Heavy oil*, or *creasote oil*, distilling below 270° (518° F.). Furnishes naphthalene. (4) *Green oil*, or *anthracene oil*, distilling above 270° . Contains anthracene and other solid hydrocarbons. The residue in the still is pitch. The light oil contains benzene, toluene and xylene, with some thiophene, phenols, pyridin, and heavy oils. It is further purified to yield various grades of commercial "*benzol*," the best of which contains about 70 per cent. of benzene, and 24 per cent. of toluene, with some xylene, cumene and thiophene.

Pure benzene is a colorless liquid, having an ethereal odor, crystallizing at 5.4° (41.7° F.), boiling at 80.5° (176.9° F.), sp. gr. 0.86 at 15° (59° F.), immiscible with water, mixing with alcohol and ether. It dissolves I, S, P, resins, caoutchouc, guttapercha, fats and many alkaloids. It is inflammable, and burns with a smoky flame.

Benzene unites directly with Cl or Br to form products of addition or of substitution. Free Cl acts only slowly upon benzene alone, but the action is much accelerated by the presence of certain chlorids, particularly Fe_2Cl_6 . The corresponding I derivatives can only be obtained indirectly. Sulfuric acid combines with it to form **benzene sulfonic acid**, $C_6H_5\cdot SO_3H$. Nitric acid converts it into nitro-benzene, $C_6H_5\cdot NO_2$, or, if fuming HNO_3 is used and the mixture boiled, into a mixture of the three dinitro-benzenes, $C_6H_4(NO_2)_2$. It is reduced to hexahydrobenzene by hydriodic acid.

Homologues of Benzene. — These may be considered as alkyl-benzenes, formed by the substitution of alkyl groups for an equivalent number of hydrogen atoms in benzene. The usual general method

of their formation indicates the constitution: they are obtained by treating a mixture of bromobenzene, ether, and the bromid or iodid of the corresponding alcoholic radical with sodium. Thus monobromo-benzene and methyl bromid yield methyl-benzene, or toluene: $\text{C}_6\text{H}_5\text{Br} + \text{CH}_3\text{Br} + \text{Na}_2 = 2\text{NaBr} + \text{C}_6\text{H}_5.\text{CH}_3$. They are also formed by the action of the alkyl chlorids upon the inferior homologues in presence of Al_2Cl_6 , or of ZnCl_2 , or Fe_2Cl_6 . Thus benzene and methyl chlorid form toluene: $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} = \text{C}_6\text{H}_5.\text{CH}_3 + \text{HCl}$. This is a general method frequently used for the introduction of alkyls into aromatic compounds, and probably depends upon the formation of intermediate organo-metallic compounds (p. 375). There are numerous other methods for their production. The superior homologues of benzene include many isomers. Thus there are:

- 1- C_7H_8 , i. e., $\text{C}_6\text{H}_5(\text{CH}_3)$ -Methyl-benzene,
 4- C_8H_{10} , i. e., three $\text{C}_6\text{H}_4(\text{CH}_3)_2$ -o-, m-, and p-Dimethyl-benzenes,
 $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)$ -Ethyl-benzene,
 8- C_9H_{12} , i. e., three $\text{C}_6\text{H}_3(\text{CH}_3)_3$ -o-, m-, and p-Trimethyl-benzenes,
 three $\text{C}_6\text{H}_4(\text{CH}_3)(\text{C}_2\text{H}_5)$ -o-, m-, and p-Methyl-ethyl benzenes,
 $\text{C}_6\text{H}_5(\text{C}_3\text{H}_7)$ -Propyl-benzene,
 $\text{C}_6\text{H}_5(\text{C}_3\text{H}_7)$ -Isopropyl-benzene,
 19- $\text{C}_{10}\text{H}_{14}$, i. e., three $\text{C}_6\text{H}_2(\text{CH}_3)_4$ -o-, m-, and p-Tetramethyl benzenes,
 three $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)_2$ -o-, m-, and p-Diethyl-benzenes,
 three $\text{C}_6\text{H}_3(\text{CH}_3)_2(\text{C}_2\text{H}_5)$ -o-, m-, and p-Dimethylethyl-benzenes,
 three $\text{C}_6\text{H}_4(\text{CH}_3)(\text{C}_3\text{H}_7)$ -o-, m-, and p-Methylpropyl-benzenes,
 three $\text{C}_6\text{H}_4(\text{CH}_3)(\text{C}_3\text{H}_7)$ -o-, m-, and p-Methylisopropyl-benzenes,
 four $\text{C}_6\text{H}_5(\text{C}_4\text{H}_9)$ -Butyl-benzenes.

The homologues of benzene are acted upon by reagents in the same manner as benzene itself. In addition, the lateral chain may be acted upon. Benzene is not acted upon notably by oxidizing agents unless they be sufficiently powerful to disrupt the molecule. But oxidants such as dilute nitric acid, or the chromic mixture, oxidize the lateral chain in the homologues of benzene, with formation of carboxylic acids. Thus methyl-benzene, $\text{C}_6\text{H}_5.\text{CH}_3$, yields benzoic acid, $\text{C}_6\text{H}_5.\text{COOH}$.

Toluene—Toluol—Methyl-benzene— $\text{C}_6\text{H}_5.\text{CH}_3$ —exists in the products of distillation of coal, wood, etc., and is a constituent of commercial benzene. It is formed synthetically by the general methods given above; or may be obtained pure by decomposition of one of the toluic acids by lime.

It is a colorless liquid, boils at 110.3° (230.5° F.), does not solidify at -20° (-4° F.), sp. gr. 0.872 at 15° (59° F.), does not mix with water, but mixes with alcohol, ether and carbon bisulfid.

Xylenes—Xylois— C_8H_{10} .—Four isomers are possible and are known: ethyl-benzene, $\text{C}_6\text{H}_5.\text{C}_2\text{H}_5$ —and ortho- (1—2), meta- (1—3),

and *para*- (1—4), **dimethyl-benzenes**, $C_6H_4(CH_3)_2$. **Ethylbenzene** is a colorless oil, b. p. 134° , obtained by fractional distillation of animal oil. The three **dimethyl benzenes** exist in coal tar and in the commercial xylene, b. p. 139° , 70 % consisting of metaxylene, and paraxylene being present in very small amount. **Mesitylene**, formed by distilling acetone or allylene with H_2SO_4 , is *p*-trimethylbenzene. **Cymene**, a liquid having a pleasant odor, present in several ethereal oils, is *p*-methylisopropyl-benzene. It is formed by the action of methyl iodid upon *p*-bromo isopropyl-benzene in presence of Na.

MONOBENZENIC HYDROCARBONS WITH UNSATURATED LATERAL CHAINS.

These are similar in constitution to the homologues of benzene, except that the lateral chains are olefins or acetylenes, in place of paraffins.

Styrolene — Cinnamene — Ethylenebenzene — Phenylethene — $C_6H_5.CH:CH_2$ —exists ready formed in essential oil of styrax. It is also formed by decomposition of cinnamic acid (p. 457), or, synthetically, by the action of a red heat upon pure acetylene, a mixture of acetylene and benzene, or a mixture of benzene and ethylene. It is a colorless liquid, has a penetrating odor, recalling those of benzene and naphthalene, and a peppery taste; boils at 143° ($289.4^\circ F.$); soluble in all proportions in alcohol and water; neutral in reaction.

Phenyl-acetylene — Acetenyl-benzene — $C_6H_5.C\equiv CH$ —is formed by heating acetophenone chlorid with KHO in alcoholic solution. It is a colorless liquid, of an aromatic odor, boils at 140° ($284^\circ F.$).

HALOID DERIVATIVES.

By the substitution of atoms of Cl, Br and I for the hydrogen of the principal and lateral chains in benzene and its superior homologues, a great number of substances are obtained, many of them forming isomeric groups.

The chlorobenzenes are: **Monochlorobenzene**: C_6H_5Cl , liquid, b. p. 132° , sp. gr. at 0° —1.128°; obtained by the action of Cl upon C_6H_6 in the cold, in presence of a little I. **Orthodichlorobenzene**: $C_6H_4Cl_{2(1-2)}$, liquid, b. p. 179° , sp. gr. 1.328 at 0° ; obtained by the action of Cl upon C_6H_6 . **Metadichlorobenzene**: $C_6H_4Cl_{2(1-3)}$, liquid, b. p. 172° , sp. gr. 1.307 at 0° ; obtained indirectly. **Paradichlorobenzene**: $C_6H_4Cl_{2(1-4)}$, crystalline, f. p. 56.4° , b. p. 170° , is the principal product of the action of Cl on C_6H_6 in presence of I. **Metatri-chlorobenzene**: $C_6H_3Cl_{3(1-2-4)}$, crystals, f. p. 17° , b. p. 213° . **Paratri-chlorobenzene**: $C_6H_3Cl_{3(1-3-5)}$, crystals, f. p. 63.4° , b. p. 208° .

Metatetrachlorobenzene: $C_6H_2Cl_{4(1-2-3-5)}$, crystals, f. p. 50° , b. p. 246° .

Paratetrachlorobenzene: $C_6H_2Cl_{4(1-2-4-5)}$, crystals, f. p. 137° , b. p. 245° .

Benzyl chlorid— $C_6H_5CH_2Cl$ —is an example of the substitution of a halogen in the lateral chain of a superior homologue of benzene. It is obtained by the action of chlorine upon boiling toluene; or of PCl_5 on benzylic alcohol. It is a colorless liquid, boils at 176° (348.8° F.), and gives off pungent vapors which excite the lachrymal secretion. It is readily oxidized to benzoic aldehyde or benzoic acid, and serves for the introduction of the radical benzyl into other molecules. The radical of benzylic alcohol ($C_6H_5.CH_2$), (p. 452) is called **benzyl**; that of benzoic acid, ($C_6H_5.CO$), **benzoyl** (p. 456). The groups C_6H_5 , called **phenyl**, and C_6H_4 , called **phenylen**, behave as radicals, corresponding to the alkyls (p. 274) and alkylens (p. 294) respectively.

BENZENIC OXYGEN COMPOUNDS.

The derivatives of benzene containing oxygen include, besides alcohols, aldehydes, ketones, acids, ethers, and anhydrides, corresponding to those of the open chain series, a class of hydroxids, the **phenols**, of which there are no aliphatic prototypes.

PHENOLS.

In the phenols the hydroxyl is substituted for the hydrogen of the benzene ring, while in the alcohols the substitution occurs in a lateral chain. Thus phenol is $C_6H_5.OH$; benzylic alcohol, $C_6H_5.CH_2OH$. All six of the hydrogen atoms of benzene may be thus replaced to form **monohydric phenols**, **dihydric phenols**, etc.

In their properties the phenols differ from the alcohols by more nearly approaching the character of the acids. On oxidation they do not furnish aldehydes or acids; they do not divide into water and hydrocarbon under the influence of dehydrating agents; they do not react with acids to form esters; they combine directly with Cl and Br to form products of substitution; they form with the metallic elements compounds more stable than similar compounds of the true alcohols.

The tertiary aliphatic alcohols are those which most closely resemble the phenols. They both contain the group $C.OH$, triply linked to other carbon atoms: $(H_3C)_2 \begin{smallmatrix} H_3C \\ \diagup \\ C.OH \end{smallmatrix}$, and $\begin{smallmatrix} =HC \\ \diagup \\ -HC \end{smallmatrix} C.CH$, and they also resemble each other in that each is only slowly and imperfectly esterified when heated to 150° with acetic acid. But, while the tertiary alcohols are readily attacked by phosphorus pentachlorid, with formation of alkyl chlorids: $(CH_3)_3 : C.OH + PCl_5 = (CH_3)_3 : C.Cl + POCl_3 + HCl$; that reagent displaces the hydroxyl of the phenols only im-

perfectly, or not at all. The products of the reaction with phenol are either phenyl phosphoric tetrachlorid: $\text{C}_6\text{H}_5.\text{OH} + \text{PCl}_5 = \text{C}_6\text{H}_5.\text{OPCl}_4 + \text{HCl}$; or a mixture of monochlorobenzene with either diphenyl phosphoric acid: $4\text{C}_6\text{H}_5.\text{OH} + \text{PCl}_5 = 2\text{C}_6\text{H}_5\text{Cl} + \text{PO}_4\text{H}(\text{C}_6\text{H}_5)_2 + 3\text{HCl}$, or triphenyl phosphate: $4\text{C}_6\text{H}_5.\text{OH} + \text{PCl}_5 = \text{C}_6\text{H}_5\text{Cl} + \text{PO}_4(\text{C}_6\text{H}_5)_3 + 4\text{HCl}$. The latter alone is produced by the action of phosphorus oxychlorid on phenol: $3\text{C}_6\text{H}_5.\text{OH} + \text{POCl}_3 = \text{PO}_4(\text{C}_6\text{H}_5)_3 + 3\text{HCl}$.

The phenols occur in nature in small quantities only; some in the vegetable world, and some in combination as ester sulfuric acids in the urine. They are mostly products of distillation of wood, coal, etc.

MONOATOMIC—MONOHYDRIC PHENOLS.

The monoatomic phenols are produced: (1) by fusing the corresponding sulfonic acids with caustic alkali: $\text{C}_6\text{H}_5.\text{SO}_3\text{K} + \text{KHO} = \text{C}_6\text{H}_5.\text{OH} + \text{K}_2\text{SO}_3$; (2) by decomposition of the diazo-compounds (p. 481) by boiling with water: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{HSO}_4 + \text{H}_2\text{O} = \text{C}_6\text{H}_5.\text{OH} + \text{N}_2 + \text{H}_2\text{SO}_4$; (3) the higher phenols are produced by heating phenol with ZnCl_2 and the alcohols, a phenolic ether being also formed. Thus phenol and methylic alcohol yield cresol and methyl-phenyl ether: $2\text{C}_6\text{H}_5.\text{OH} + 2\text{H}.\text{CH}_2\text{OH} = \text{C}_6\text{H}_4.\text{OH}.\text{CH}_3 + \text{C}_6\text{H}_5.\text{O}.\text{CH}_3 + 2\text{H}_2\text{O}$.

The phenols are reduced to hydrocarbons by heating with zinc dust. Their ring-hydrogen is readily replaceable by other elements or groups to form haloid, nitro, amido derivatives, etc. Their hydroxyl hydrogen is also readily replaceable by alkyls to produce ethers, by Na, K, and Ca to produce phenates, and by acidyls to produce phenyl esters (p. 446). The phenols combine with the diazo compounds to produce azo- and diazo dyes, and with phthalic acid to produce phthaleïns.

Phenol—Benzophenol—Phenyl hydroxid—Phenic acid—Carbolic acid— $\text{C}_6\text{H}_5.\text{OH}$ —exists in considerable quantity in coal- and wood-tar, and in small quantity in castoreum and, in combination, in the urine. It is produced in the intestine.

It is formed: (1) by fusing sodium-phenyl sulfid with excess of alkali: $\text{C}_6\text{H}_5.\text{NaS} + \text{NaHO} = \text{C}_6\text{H}_5.\text{OH} + \text{Na}_2\text{S}$; (2) by heating phenyl iodid and potassium hydroxid at 320° (608°F.): $\text{C}_6\text{H}_5\text{I} + \text{KHO} = \text{C}_6\text{H}_5.\text{OH} + \text{KI}$; (3) by heating together salicylic acid and quicklime: $\text{C}_6\text{H}_4.\text{OH}.\text{COOH} + \text{CaH}_2\text{O}_2 = \text{C}_6\text{H}_5.\text{OH} + \text{CaCO}_3 + \text{H}_2\text{O}$; (4) by total synthesis from acetylene, through benzene (p. 433), and its sulfonic acid; (5) by decomposition of the phenylic esters by alkalies. Thus salol yields phenol and salicylic acid: $\text{C}_6\text{H}_4.\text{OH}.\text{COO}(\text{C}_6\text{H}_5) + \text{KHO} = \text{C}_6\text{H}_5.\text{OH} + \text{C}_6\text{H}_4.\text{OH}.\text{COOK}$; (6) by dry distillation of benzoin. "Synthetic phenol," prepared by method (4), is now manufactured. "Carbolic acid" is obtained from the "middle oil" of gas tar (p. 440).

It is purified by conversion into potassium phenate, $C_6H_5.OK$, which is crystallized, decomposed by HCl , and the liberated phenol recrystallized and distilled.

Phenol is extensively used, not only as an antiseptic, but also in the manufacture of numerous derivatives, including medicinal compounds, dyes and explosives.

Phenol crystallizes in long, colorless needles, fuses at 43° (109.4° F.), boils at 183° (361.4° F.), sp. gr. 1.084 at 0° (32° F.), has a characteristic odor, and an acrid, burning taste, soluble in 15 parts of water at 20° (68° F.), very soluble in alcohol and in ether, neutral in reaction. It may be distilled without decomposition.

Its vapor is reduced to benzene by heating with Zn . It combines with H_2SO_4 to form o-, and p-phenol sulfonic acids. With HNO_3 it forms 2-4-6-trinitrophenol. Heated with sulfuric and oxalic or arsenic acid, it yields several triphenyl-methane dyes, among which are corallin, rosolic acid, peonin, azulin, aurin, and phenicin.

Analytical Characters—(1) Its peculiar odor. (2) Mix with one quarter volume of NH_4HO ; add two drops of sodium hypochlorite solution, and warm: a blue or green color. Add HCl to acid reaction: turns red. (3) Add two drops of the liquid to a little HCl , and then a drop of HNO_3 : a purple red color. (4) Boil with HNO_3 so long as red fumes are given off, neutralize with KHO : a yellow, crystalline precipitate. (5) Heat with Millon's reagent: a yellow ppt., forming a red solution in HNO_3 . (6) With solution of $FeSO_4$: a lilac color. (7) Add excess of bromin water: a yellowish-white precipitate. This compound, tribromophenol, $C_6H_2Br_3OH$, is the form in which phenol is quantitatively determined; 100 parts of it correspond to 29.8 parts of phenol. (8) Moisten a pine shaving with the liquid, then with HCl , to which a trace of $KClO_3$ has been added immediately before use, and expose to sunlight: a fine blue color. The test could be tried also with a solution of phenol, and with the acid one, as only certain varieties of pine are suitable. (Pine-shaving reaction. See also Pyrrole.)

Toxicology.—Carbolic acid is an active poison and corrosive. It has caused death in a dose of 1.5 gram. The average duration of fatal cases is 2-8 hours. Death may occur in 3-5 minutes from collapse. It causes a burning sensation, soon followed by intense pain and cauterization of all parts with which it comes in contact. The skin in which it produces is at first white, after a few minutes; later it turns darker and, when the eschar separates, a brown stain remains, which persists for many days. Vomiting usually occurs, the vomited matters, as well as the breath, having the odor of carbolic acid. The patient soon becomes unconscious, and death is from collapse or in coma. The urine, normal in color when first voided, soon becomes

olive-green, brown, or even black in color. The treatment consists in administration of albumen, saccharated lime, sodium sulfate, or strong alcohol, followed by lavage.

Phenates.—*Carbolates.*—The hydroxyl hydrogen of phenol is replaceable by certain metals and by alkyls to form phenates and phenyl ethers. When phenol and KHO are heated together, **potassium phenate**, C_6H_5OK , is formed. This, when treated in alcoholic solution with $HgCl_2$, produces **mercuric phenate**, $(C_6H_5O)_2Hg$, a yellow, crystalline solid which has been used in medicine.

Phenol Esters.—The H of the OH of phenol is replaceable by either alkyls or acidyls. With the former phenol plays the part of an acid, and therefore the resulting compounds are the phenol esters, corresponding to the metallic phenates. But, although phenol is not an alcohol, the radical phenyl $(C_6H_5)'$ of which it is the hydroxid, is in all respects equivalent to the alkyls, of which the monohydric alcohols are the hydroxids. Therefore the phenol esters, such as $C_6H_5.O.CH_3$, are also the phenyl ethers (p. 464). The phenyl esters, on the other hand, may be considered as derivable from phenol by substitution of acidyls for hydroxyl hydrogen: $C_6H_5.O.(OC.CH_3)$, or as derivable from the acids by substitution of phenyl for carboxyl hydrogen: $CH_3.COO(C_6H_5)$. The phenyl esters are formed by the action of the acidyl chlorids upon the phenols, or upon their metallic derivatives: $C_6H_5.OH + CH_3.COCl = CH_3.CO_2.C_6H_5 + HCl$, or, $C_6H_5.OK + CH_3.COCl = CH_3.CO_2.C_6H_5 + KCl$, as the aliphatic esters are formed by the action of acidyl halids upon the alcohols or upon the alcoholates (p. 359).

Cresols—**Cresylols**—**Cresylic acids**—**Benzylic or cresylic phenols**— $C_6H_4\begin{smallmatrix} CH_3 \\ \diagdown \\ OH \end{smallmatrix}$ —108.—Of the three possible compounds, two, the para and ortho, accompany phenol in coal-tar, from which they may be separated by fractional distillation. They are more readily obtained pure from toluene. **Creolin**—an antiseptic less poisonous than phenol, consists chiefly of cresols. **Lysol** is impure paracresol, mixed with fat and saponified.

Creasote—**Creasotum** (U. S.)—is a complex mixture containing phenol, cresol, **creasol**, $C_8H_{10}O_2$, **guaiacol**, $C_7H_8O_2$ (see pyrocatechol), and other substances, obtained from wood-tar, and formerly extensively used as an antiseptic. It is an oily liquid, colorless when freshly prepared, but becoming brownish on exposure to light. It has a burning taste and a strong, peculiar odor. It boils at 203° (397.4° F.), and does not solidify at -27° (-16.6° F.).

Xenols—**Xylenols**.—Theoretically there are six possible xenols which are **dimethyl phenols**, $C_6H_3(CH_3)_2OH$; two derivable from orthoxylene, three from metaxylene and one from paraxylene. They

have all been produced synthetically. There are also three possible xenols which are **ethyl phenols**, $C_6H_4(C_2H_5)OH$.

Thymol—3-Methyl-6-isopropyl phenol—Cymylic phenol— $C_6H_3(OH)_{(1)}(CH_3)_{(3)}(C_3H_7)_{(6)}$,—exists, accompanying cymene and thymene, $C_{10}H_{16}$, in essence of thyme, from which it is obtained. It is also prepared synthetically from cuminic aldehyde, $C_6H_4(CHO)_{(1)}(C_3H_7)_{(4)}$.

It crystallizes in large, transparent, rhombohedral tables; has a peppery taste, and an agreeable, aromatic odor. It fuses at 44° (111.2° F.), and boils at 230° (446° F.); is sparingly soluble in water, very soluble in alcohol and ether. With the alkalies it forms definite compounds, which are very soluble in water. Its reactions are very similar to those of phenol.

Thymol is an excellent deodorizing and antiseptic agent, possessing the advantage over phenol of having itself a pleasant odor.

Aristol is diiodo-thymol, a dibenzenic compound, produced by the action of a solution of I in KI upon an aqueous solution of thymol in the presence of KHO. It is an inodorous, yellowish-red powder, insoluble in H_2O , very sparingly soluble in alcohol, readily soluble in ether and in chloroform. It is decomposed by heat and by light and is said to be a non-poisonous antiseptic.

Carvacrol—2-Methyl-5-isopropyl phenol— $C_6H_3(OH)_{(1)}(CH_3)_{(3)}(C_3H_7)_{(3)}$ —an isomere of thymol, exists in many essential oils, and is obtained by the action of iodine upon camphor; by the action of potash in fusion upon cymene sulfonic acid, $C_{10}H_{13}SO_3H$; or by a transposition of the atoms of another isomere, **carvol**, which exists in caraway oil. It is an oil, boiling at 233° – 235° (451.4° – 455° F.). Heated with P_2O_5 , it yields orthocresol.

SUBSTITUTED PHENOLS.

Phenol is a monosubstituted derivative, and hence still contains five H atoms which may be replaced by other elements or radicals, to produce di- or tri- or poly-substituted derivatives of benzene, which will be ortho, meta or para, etc., according to the relations of the introduced groups to the OH, already existing in phenol, or to the C_nH_{2n+1} and OH groups in its superior homologues.

Chlorophenols.—The three monochlorinated compounds are obtainable from the corresponding chloranilins. **Orthochlorophenol** (1–2) is a colorless liquid, boils at 175° – 176° (347° – 348.8° F.), converted into pyrocatechol by KHO. **Metachlorophenol** (1–3) is a liquid, boiling at 214° (417.2° F.). KHO converts it into resorcinol. **Parachlorophenol** (1–4) is a crystalline solid, fusible at 37° (98.6° F.), converted into quinol by fusion with KHO. Di-, tri-, and penta-chlorophenols are also known.

Bromophenols correspond in method of formation and properties with the Cl derivatives. **2-4-6 Tribromophenol**— $C_6H_2.OH.Br_3$ —is the precipitate formed on adding bromin water to phenol solution. It forms white crystals, fusing at 92° ($197.6^\circ F.$), insoluble in water, soluble in alcohol and ether. It is used as an antiseptic in diphtheria under the name **Bromol**. Paramonochlorophenol and orthomono-bromophenol have been used for the same purpose.

Iodophenols are formed by the action of iodine and K_2S upon phenol in the presence of excess of alkali, or from the corresponding amidophenols. Like the chlorin and bromin derivatives, they yield the corresponding diphenol by the action of KHO in fusion. A tri-iodophenol, formed by the action of solution of I in K_2S upon an alkaline solution of phenol, has been proposed as a substitute for iodoform under the name **annidalin**. (See also pp. 459, 464, 472.)

DIATOMIC, OR DIHYDRIC PHENOLS.

Diatomic phenols are derived from the benzenic hydrocarbons by the substitution of two (OH) groups for two atoms of hydrogen. In obedience to the laws of substitution already discussed, three such compounds exist, corresponding to each hydrocarbon.

Pyrocatechol—*Pyrocatechin*—*Oxyphenic acid*—*Orthodioxo-benzene*— $C_6H_4(OH)_2$ (1, 2) is obtained from catechin or from morintannic acid by dry distillation; also by the action of KHO on orthochlor- or orthiodo-phenol, or by decomposing its methyl ether, **guaiacol**, by HI at 200° ($392^\circ F.$). It crystallizes in short, square prisms; fuses at 104° ($219.2^\circ F.$), and boils at 245.5° ($473.9^\circ F.$). Readily soluble in water, alcohol, and ether. Its aqueous solution gives a dark green color with Fe_2Cl_6 solution, changing to violet on addition of NH_4HO , $NaHCO_3$, or tartaric acid. Its acid sulfuric ester exists in the urine.

Monomethyl-pyrocatechuic Ether—**Guaiacol**— $C_6H_4.OH.(OCH_3)$ (2)—exists in beech-wood tar, from which an impure (60-90%) guaiacol is obtained as a yellowish liquid, sp. gr. 1.133, boiling at 206° - 207° , by distillation. Pure guaiacol is obtained from this by crystallization at low temperature; by heating pyrocatechol with potassium-methyl sulfate and KHO ; also from vanillin (p. 454), and from veratrol. It is a crystalline solid, fuses at 33° ($91.4^\circ F.$), boils at 205° ($401^\circ F.$), soluble in 50 parts of water. Guaiacol is used in the treatment of phthisis both on account of its germicidal action, and upon the theory that it forms compounds with the toxalbumins (q. v.), which are readily eliminated. It is also used in numerous forms of combination: in its carbonic esters, as **styracol**=cinnamyl-guaiacol, as **benzosol**=benzoyl-guaiacol, as **thiocol**=guaiacol-potassium sulfonate, and in combination with salicylic acid.

Dimethyl-pyrocatechuic Ether—Veratrol— $C_6H_4(OCH_3)_{2(1-2)}$ —is an oil, crystallizing at 15° (59° F.), formed by distilling veratric acid (p. 460), or by acting upon the potassium salt of guaiacol with methyl iodid.

Resorcinol—Resorcin—Metadioxy-benzene— $C_6H_4(OH)_{2(1,3)}$ is obtained by the action of fused KHO on metachlor- or iodophenol. It is also prepared by dry distillation of extract of Brazil wood.

It forms short, thick, colorless and odorless, rhombic prisms. Fuses at 104° (219.2° F.), and boils at 271° (519.8° F.). It is very soluble in water, alcohol, and ether. Its aqueous solution is neutral in reaction, and intensely sweet. With Fe_2Cl_6 its solutions assume a dark-violet color, which is discharged by NH_4HO . Its ammoniacal solution, by exposure to air, assumes a pink color, changing to brown and, on evaporation, green and dark blue. Heated with phthalic anhydrid at 195° (383° F.) it yields **fluorescein** (p. 451). It dissolves in fuming H_2SO_4 , forming an orange-red solution, which becomes darker, changes to greenish-black, then to pure blue, and finally to purple on being warmed.

Resorcinol, heated with sodium nitrite and H_2O to about 150° (302° F.) yields a blue pigment known as **lacmoid**, which behaves like litmus with acids and alkalies, but is more sensitive.

Quinol—Hydroquinone—Paradioxy-benzene— $C_6H_4(OH)_{2(1,4)}$ is formed by fusing paraiodo-phenol with KHO at 180° (356° F.), by dry distillation of oxysalicic acid or of quinic acid, and by the action of reducing agents on quinone. It forms colorless, rhombic prisms, which fuse at 169° (336.2° F.). Readily soluble in water, alcohol, or ether. Its aqueous solution is turned red-brown by NH_4HO . Oxidizing agents convert it into quinone.

Orsinol—Orsin—Dimetadioxy toluene— $C_6H_3(CH_3)_{(1)}(OH)_{(3)}(OH)_{(2)}$ —a homologue of resorcinol, exists in nature in those lichens which are used as sources of archil and litmus (*Rocella tinctoria*, etc.). It crystallizes in six-sided prisms; is sweet; readily soluble in water, alcohol, or ether; fuses at 58° (136.4° F.). Its aqueous solution is colored violet-blue by Fe_2Cl_6 . It unites with NH_3 to form a compound which absorbs O from the air, and is converted into **orcein**, $C_7H_7NO_3$; a dark-red or purple body, which is the chief constituent of the dye-stuff known as archil, cudbear, French purple, and litmus.

TRIATOMIC, OR TRIHYDRIC PHENOLS.

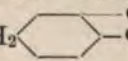
Phloroglucin— $C_6H_3(OH)_{3(1,3,5)}$ —is obtained by the action of potash upon phloretin, quercitrin, maelurin, catechin, kino, etc. It crystallizes in rhombic prisms, containing 2Aq; is very sweet; and very soluble in water, alcohol, and ether.

Pyrogallol—*Pyrogallie acid*— $C_6H_3(OH)_{3(1,2,3)}$ —is formed when gallic acid (p. 461) is heated to 200° (392° F.). It crystallizes in white needles; neutral in reaction; very soluble in water; very bitter; fuses at 132° (238° F.); boils at 210° (410° F.); poisonous. Its most valuable property is that of absorbing oxygen, for which purpose it is used in the laboratory in the form of a solution of potassium pyrogallate.

When pyrogallol is heated with half its weight of phthalic anhydrid for several hours at 190° – 200° (374° – 392° F.) it yields **pyrogallol phthalein**, or **gallein**, a brown-red powder (or green crystals) which dissolves with a brown color in neutral solutions, the color changing to red with a faint excess of alkali.

Oxyhydroquinone— $C_6H_3(OH)_{3(1,2,4)}$ —is produced by fusing quinone with KHO. It is crystalline, fuses at 140° (284° F.), very soluble in water and in ether.

UNSATURATED PHENOLS.

These are derived from the benzenic hydrocarbons with unsaturated lateral chains (p. 442). Olefin monoxybenzenes, dioxybenzenes, trioxybenzenes, and a tetroxybenzene are known. They are aromatic oils of high boiling points, many derived from various plants. Included in this class are: **Chavicol**, **p-Allyl phenol**— $C_6H_4\cdot OH\cdot(CH_2\cdot CH:CH_2)_{(4)}$ —occurs in an oil from certain peppers. Its isomere, **p-Propenyl phenol**, $C_6H_4\cdot OH\cdot(CH:CH\cdot CH_3)_{(4)}$, is **p-anol**, whose methylic ether, $C_6H_4\cdot O(CH_3)\cdot(CH:CH\cdot CH_3)_{(4)}$, **p-propenyl anisol**, or **anethol**, exists in the oils of anise, estragon and fennel. Among the diphenols is **eugenol**, $C_6H_3\cdot(CH_2\cdot CH:CH_2)_{(1)}\cdot(OCH_3)_{(3)}\cdot(OH)_{(4)}$, allyl 3-4-guaiacol, an essential oil from pimenta, eugenia, and certain peppers. The corresponding dimethyl compound exists in bay-oil. **Safrol**, Allyl 3-4 pyrocatechol methylene ether, $CH_2:CH\cdot CH_2\cdot$  CH_2 , is present in oil of saffras, and oil of illicium. **Apiol**, from oil of parsley, is a complex methylene ether, corresponding to allyl tetraoxybenzene, $C_6H\cdot(OH)_4\cdot CH_2\cdot CH:CH_2$.

PHENOL DYES.

Aurin— $C_{19}H_{14}O_3$, and **Rosolic acid**— $C_{20}H_{16}O_3$ —are substances existing in the dye obtained by the action of oxalic acid upon phenol in presence of H_2SO_4 , known as **corallin**, or **pæonin**, which communicates to silk or wool a fine yellow-red color.

Aurin crystallizes in fine, red needles from its solution in HCl.

It is insoluble in H_2O , but soluble in HCl , alcohol, and glacial acetic acid. It forms a colorless compound with potassium bisulfite.

Phthaleïns.—These substances are produced by heating the phenols with phthalic anhydrid, $C_6H_4(CO)_2O$, water being at the same time eliminated.

Their constitution is that of a benzene nucleus, two of whose H atoms have been replaced by two acetone groups (CO), whose remaining valences attach them to two phenol groups by exchange with an atom of hydrogen (see p. 504).

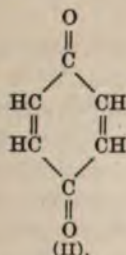
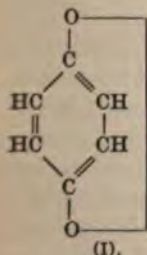
Thus **phenol-phthaleïn**, the simplest of the group, has the constitution, $C_6H_4 \begin{matrix} \diagup CO-C_6H_4(OH) \\ \diagdown CO-C_6H_4(OH) \end{matrix}$. Phenol-phthaleïn is a yellow, crystalline powder, insoluble in water, but soluble in alcohol. Its alcoholic solution, perfectly colorless if neutral, assumes a brilliant magenta-red in the presence of an alkali. This property renders phenol-phthaleïn very valuable as an *indicator* of reaction.

Resorcinol-phthaleïn — Fluoresceïn — $C_{20}H_{12}O_5$ — bears the same relation to resorcinol that phenol-phthaleïn does to phenol, and is obtained from resorcinol by a corresponding method. It is a dark-brown crystalline powder, which dissolves in ammonia to form a red solution, exhibiting a most brilliant green fluorescence. A tetrabromo-derivative of fluoresceïn is used as a dye under the name **eosin**.

QUINONES.

The quinones are benzene derivatives in which two atoms of hydrogen are replaced by two oxygen atoms. The attachment of the $-O.O-$ group is either ortho- or para-, never meta-. **Ortho-quinones** of the polybenzenic series, such as β naphthoquinone and anthraquinone (p. 499), are well-known compounds, but the monobenzenic ortho-quinones are only known in their derivatives.

The **monobenzenic para-quinones** may be considered either as peroxids, the bonds of the benzene ring remaining intact (Formula I),



or they may be considered as ringketones (Formula II), in which the two CO groups form a part of an oxidized hydroaromatic ring (p. 486). The former view is favored by the facts that the quinones are strong oxidizing agents, as are the peroxids in general, and that they yield monosubstituted derivatives by replacement

of their oxygen by univalents, as benzoquinone forms p-dioxyben-

zene, $(\text{HO})\text{C} \begin{smallmatrix} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{CH.CH} \end{smallmatrix} \text{C}(\text{OH})$ on reduction, and p-dichlorobenzene, $\text{ClC} \begin{smallmatrix} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{CH.CH} \end{smallmatrix} \text{CCl}$, by the action of PCl_5 . On the other hand, the existence of the $\text{CO} =$ group in the quinones is indicated by the fact that they readily form oxims with hydroxylamin, a reaction characteristic of compounds containing $\text{CO} =$ (p. 299), as benzoquinone forms quinone dioxim, $\text{HO.NC} \begin{smallmatrix} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{CH.CH} \end{smallmatrix} \text{CN.OH}$; and if, by reason of its oxidation of phenylhydrazin, benzoquinone forms no phenylhydrazone (p. 485) such compounds are formed by the naphthoquinones.

The quinones form a number of derivatives, by the introduction of alkyl, halogen, amido-, nitro, etc., groups for their hydrogen or oxygen. Among these are the **anils**, formed by substitution of $=\text{N.C}_6\text{H}_5$ for O, from which, in turn, an important series of blue and green dyes, the **indooanilin** or **indulin dyes** are derived.

Quinone — Benzoquinone — $\text{C}_6\text{H}_4: \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix}$ — is formed by the action of oxidants upon a variety of p-benzene derivatives, but best by limited oxidation of quinic acid. It crystallizes in golden-yellow prisms, f. p. 116° (240.8° F.), sublimes at ordinary temperatures, sparingly soluble in cold water, readily soluble in hot water, alcohol and ether. It has a peculiar, pungent odor, stimulates the lachrymal secretion, and irritates the skin. Reducing agents convert it into quinol.

AROMATIC ALCOHOLS.

The alcohols (p. 284) corresponding to this series of hydrocarbons are isomeric with the phenols. They contain the characterizing group of the primary alcohols, CH_2OH ; once if the alcohol be monoatomic, twice if diatomic, etc., and they yield on oxidation, first an aldehyde and then an acid. Thus: $\text{C}_6\text{H}_5.\text{CH}_2\text{OH} =$ benzylic alcohol; $\text{C}_6\text{H}_5.\text{CHO} =$ benzoic aldehyde; $\text{C}_6\text{H}_5.\text{COOH} =$ benzoic acid.

They are capable of yielding isomeric products of further substitution, ortho, para, or meta.

Benzylic Alcohol — Benzoic Alcohol — Benzyl Hydrate — $\text{C}_6\text{H}_5.\text{CH}_2\text{OH}$ — does not exist in nature, and is of interest chiefly as corresponding to two important compounds, benzoic acid and benzoic aldehyde (oil of bitter almonds). It is obtained by the action of potassium hydroxid upon oil of bitter almonds, or by slowly adding sodium amalgam to a boiling solution of benzoic acid.

It is a colorless liquid; boils at 206.5° (403.7° F.); has an aromatic odor; is insoluble in water, soluble in all proportions in alcohol, ether, and carbon bisulfid. By oxidation it yields, first, benzoic

aldehyde, $C_6H_5.CHO$; and afterward, benzoic acid, $C_6H_5.COOH$. By the same means it may be made to yield products similar to those obtained from the alcohols of the saturated hydrocarbons.

Secondary and tertiary aromatic alcohols are also known, such as **phenyl-methyl carbinol**, $C_6H_5.CHOH.CH_3$, and **phenyl-dimethyl carbinol**, $C_6H_5.CO(CH_3)_2$ (p. 285). The secondary alcohols yield ketones on oxidation (p. 455).

Di- and tri-hydric alcohols, such as the **xylylene glycols**, $C_6H_4.(CH_2OH)_2$ (p. 294), and **mesitylene glycerol**, $C_6H_3.(CH_2OH)_3$ (1-3-5), are also known, as well as alcohols with unsaturated lateral chains, such as **cinnamic alcohol**, $C_6H_5.CH:CH.CH_2OH$, which occurs as its cinnamic ester in *storax*. It oxidizes to cinnamic aldehyde (p. 454) and cinnamic acid (p. 457).

ALPHENOLS, OR OXYPHENYL ALCOHOLS.

These substances are intermediate in function between the alcohols and the phenols, and contain both substituted groups OH and CH_2OH .

Saligenin—*o-Oxybenzylic Alcohol*— $C_6H_4 \begin{smallmatrix} \diagup CH_2OH \\ \diagdown OH \end{smallmatrix}$ —is obtained from salicin (p. 467) in large, tabular crystals; quite soluble in alcohol, water, and ether. Oxidizing agents convert it into salicylic aldehyde, which by further oxidation yields salicylic acid. It is also formed by the action of nascent hydrogen on salicylic aldehyde.

ALDEHYDES.

The aromatic aldehydes (p. 299) are the first products of oxidation of the aromatic alcohols. **Monaldehydes** containing one CHO group and **dialdehydes** containing two such groups are known.

The monaldehydes are formed: (1) By oxidation of the alcohols; (2) by decomposition of the alcohol bichlorids by water: $C_6H_5.CHCl_2 + H_2O = C_6H_5.CHO + 2HCl$. (3) By oxidation of the alcohol monochlorids by lead nitrate: $C_6H_5.CH_2Cl + O = C_6H_5.CHO + HCl$. (4) By the action of chromyl chlorid, CrO_2Cl_2 , upon the hydrocarbons, and decomposition of the addition compound by water.

Benzoic Aldehyde—**Benzoyl hydrid**— $C_6H_5.CHO$ —is the main constituent of oil of bitter almonds, although it does not exist in the almond (see p. 466). It is formed, along with hydrocyanic acid and glucose, by the action of water upon amygdalin. It is also formed by the general methods given above; by the dehydration of benzylic alcohol; by the dry distillation of a mixture in molecular proportions of calcium benzoate and formate; by the action of nas-

cent hydrogen upon benzoyl cyanid, etc. It is obtained from bitter almonds. The crude oil contains, besides benzoic aldehyde, hydrocyanic and benzoic acids and benzoyl cyanid.

It is a colorless oil, having an acrid taste and the odor of bitter almonds; sp. gr. 1.050; boils at 179.4° (354.9° F.); soluble in 30 parts of water, and in all proportions in alcohol and ether. Oxidizing agents convert it into benzoic acid, a change which occurs by mere exposure to air. Nascent hydrogen converts it into benzylic alcohol. With Cl and Br it forms benzoyl chlorid or bromid. H_2SO_4 dissolves it when heated, forming a purple-red color, which turns black if more strongly heated. It forms a series of products of substitution, haloid, nitro, amido, etc.

When perfectly pure, benzoic aldehyde exerts no deleterious action when taken internally; owing, however, to the difficulty of completely removing the hydrocyanic acid, the substances usually sold as *oil of bitter almonds*, *ratafia*, and *almond flavor*, are almost always poisonous, if taken in sufficient quantity. They may contain as much as 10–15 per cent. of hydrocyanic acid, although said to be "purified." The presence of the poisonous substances may be detected by the tests given on page 392.

Salicylic Aldehyde—*Salicyl hydrid*—*Salicylal*—*Salicylous acid*—*o-Oxybenzaldehyde*— $\text{C}_6\text{H}_4(\text{OH})(\text{CHO})_{(a)}$ —exists in the flowers of *Spiræa ulmaria*, and is the principal ingredient of the essential oil of that plant. It is best obtained by oxidizing salicin (p. 467).

It is a colorless oil; turns red on exposure to air; has an agreeable, aromatic odor, and a sharp, burning taste; sp. gr. 1.173 at 13.5° (56.3° F.); boils at 196.5° (385.7° F.); soluble in water, more so in alcohol and in ether.

It is, as we should suspect from its origin, a substance of mixed function, possessing the characteristic properties of aldehyde and phenol. It produces a great number of derivatives, some of which are salts or esters, such as *p-methoxybenzaldehyde*, or *anisic aldehyde*, $\text{C}_6\text{H}_4(\text{CHO})(\text{OCH}_3)_{(a)}$, a product of oxidation of *anethol* (p. 450).

Vanillin—*Methylprotocatechuic Aldehyde*—*m-Methoxy-p-oxybenzaldehyde*— $\text{C}_6\text{H}_3\text{CHO}(\text{O.CH}_3)_{(3)}(\text{OH})_{(a)}$ —a methylated dioxybenzaldehyde, is the odoriferous principle of vanilla. It is produced artificially by oxidation of *coniferin*, $\text{C}_{16}\text{H}_{22}\text{O}_8$, a glucosid occurring in coniferous plants (p. 466). It crystallizes in needles, fuses at 80° (176° F.), is sparingly soluble in water, readily soluble in alcohol or ether. It has a pungent taste and a persistent odor of vanilla. On exposure to air it becomes partly oxidized to *vanillic acid*, $\text{C}_8\text{H}_8\text{O}_4$.

Cinnamic Aldehyde— β *Phenyl-acrolein*— $\text{C}_6\text{H}_5\text{CH:CH.CHO}$ —is an example of the aromatic aldehydes with unsaturated lateral

chains. It is the chief constituent of oil of cinnamon; and is a colorless, aromatic oil, boiling at 247° (470.6° F.). It oxidizes readily to cinnamic acid (p. 457).

KETONES.

The aromatic ketones (p. 307) are produced by the oxidation of the secondary aromatic alcohols (p. 453); $2\text{C}_6\text{H}_5.\text{CHOH}.\text{CH}_3 + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{C}_6\text{H}_5.\text{CO}.\text{CH}_3$; or by the action of caustic potash upon the aromatic β ketone-carboxylic acids (p. 464): $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_2.\text{COOH} + 2\text{KHO} = \text{C}_6\text{H}_5.\text{CO}.\text{CH}_3 + \text{H}_2\text{O} + \text{K}_2\text{CO}_3$. **Monoketones**, **diketones** and **triketones**, containing one, two and three lateral chains with CO groups, are known. The **monoketones**, also called **phenones**, consist of a closed chain hydrocarbon group united to an open chain one by the group (CO)''. They may also be considered as benzene, into which fatty acid radicals have been substituted for hydrogen (see p. 504).

Phenyl-methyl Ketone—Acetyl benzene—Acetophenone—Hypnone— $\text{C}_6\text{H}_5.\text{CO}.\text{CH}_3$ —is obtained by distilling a mixture of calcium benzoate and acetate; by the action of zinc-methyl upon benzoyl chlorid; or by the action of acetyl chlorid or bromid upon benzene in the presence of aluminium chlorid. It forms large crystalline plates, fusible at 20° (68° F.). It has been used as a hypnotic.

Acetophenone Oxim— $\text{C}_6\text{H}_5.\text{C}:(\text{N}.\text{OH}).\text{CH}_3$ —is isomeric with acetanilid, $\text{C}_6\text{H}_5.\text{NH}(\text{CO}.\text{CH}_3)$, and is converted into that substance by the action of concentrated H_2SO_4 (p. 475).

AROMATIC CARBOXYLIC ACIDS.

All six of the hydrogen atoms of benzene are replaceable by carboxyl groups, with formation of monocarboxylic acids, dicarboxylic acids, etc. There are also three series, o-, m-, and p-, of the bi-, tri-, and tetracarboxylic acids, and of the monocarboxylic acids above the first. These acids may be obtained by oxidation of the corresponding alcohols, or aldehydes, where these are known. Like the aliphatic acids, they may be considered as being derived from the hydrocarbons by substitution of hydroxyl and oxygen for hydrogen in a lateral chain (p. 282).

MONOCARBOXYLIC AROMATIC ACIDS—BENZOIC SERIES.

These acids are formed by many methods, among which the most important are: (1) By oxidation of the lateral chain in hydrocarbons

homologous with benzene. Thus toluene yields benzoic acid: $2\text{C}_6\text{H}_5\cdot\text{CH}_3 + 3\text{O}_2 = 2\text{C}_6\text{H}_5\cdot\text{COOH} + 2\text{H}_2\text{O}$; (2) by oxidation of the corresponding alcohols and aldehydes; (3) by the action of sodium and carbon dioxid upon the monobromobenzenes: $\text{C}_6\text{H}_5\text{Br} + \text{CO}_2 + 2\text{Na} = \text{NaBr} + \text{C}_6\text{H}_5\cdot\text{COONa}$; (4) by decomposition of the aromatic acid nitrils by acids or alkalies (pp. 328, 428): $\text{C}_6\text{H}_5\cdot\text{CN} + \text{KHO} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\cdot\text{COOK} + \text{NH}_3$. (5) By fusion of the aromatic sulfonic acids with sodium formate: $\text{C}_6\text{H}_5\cdot\text{SO}_3\text{Na} + \text{H}\cdot\text{COONa} = \text{C}_6\text{H}_5\cdot\text{COONa} + \text{NaHSO}_3$.

The acids of this series form many derivatives. In some of these the carboxyl is modified, leaving either the radical **benzoyl**, $\text{C}_6\text{H}_5\cdot\text{CO}$, as in **benzamid**, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2$, or the trivalent group **benzenyl**, $\text{C}_6\text{H}_5\cdot\text{C}$, as in **benzenyl-amidin**, $\text{C}_6\text{H}_5\cdot\text{C} \begin{smallmatrix} \text{NH}_2 \\ \diagup \\ \text{NH} \end{smallmatrix}$. In others the substitution occurs in the benzene ring, as in the oxy-, halogen-, and nitro-benzoic acids, etc., e. g. **anthranilic**, or **o-amido-benzoic acid**, $\text{C}_6\text{H}_4\cdot\text{COOH}_{(1)}(\text{NH}_2)_{(2)}$.

Benzoic Acid— $\text{C}_6\text{H}_5\cdot\text{COOH}$ —exists in benzoin, tolu balsam, castoreum, and in several resins. It is obtained by the general methods given above; also from benzoin, and from the urine of herbivorous animals. The urine contains hippuric acid (p. 479), which, on decomposition, yields benzoic acid. Conversely, when benzoic acid is taken into the body in moderate doses it is eliminated as hippuric acid.

Benzoic acid crystallizes in white, transparent plates, odorless, sparingly soluble in cold water, readily soluble in hot water, in alcohol and in ether; fuses at 120° (248° F.), boils at 250° (482° F.), and sublimes at temperatures below its boiling point. Benzoic acid is not attacked by HNO_3 . Heated with lime, it yields benzene and calcium carbonate: $\text{C}_6\text{H}_5\cdot\text{COOH} + \text{CaH}_2\text{O}_2 = \text{C}_6\text{H}_6 + \text{CaCO}_3 + \text{H}_2\text{O}$. The benzoates are all soluble, the least soluble being the ferric salt.

Homologues of Benzoic Acid.—These are of two kinds: (1) Those in which the carboxyl and hydrocarbon groups replace different hydrogen atoms, the **alkyl-benzoic acids**, as **cumic acid**, or **p-isopropyl benzoic acid**, $\text{C}_6\text{H}_4\cdot(\text{C}_3\text{H}_7)_{(1)}(\text{COOH})_{(2)}$. (2) Those in which the carboxyl is separated from the benzene ring by a hydrocarbon group, the **phenyl fatty acids**, as **phenyl-acetic acid**, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{COOH}$. In the terms above the first of this series there are place isomeres according to the distance from the ring in which the carboxyl is introduced. Thus α **phenyl-propionic acid**, $\text{C}_6\text{H}_5\cdot\text{CH} \begin{smallmatrix} \text{COOH} \\ \diagup \\ \text{CH}_3 \end{smallmatrix}$, and β **phenyl-propionic acid**, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$.

POLYCARBOXYLIC AROMATIC ACIDS.

The di-, tri-, tetra-, penta-, and hexa-carboxylic aromatic acids are derived from benzene by substitution of from two to six car-

boxyls for hydrogen atoms. Of the superior homologues there exist a number of isomeres, increasing with the number of carbon atoms, according as the carboxyls are attached to the benzene ring, as in the phthalic acids, or are contained in lateral chains, as in **phenyl-malonic acid**, $C_6H_5.CH(COOH)_2$, and varying further by differences in orientation either in the benzene or the lateral chains.

Phthalic Acids— $C_6H_4(COOH)_2$ —Ortho-, meta-, and para-phthalic acids are produced by oxidation of the corresponding bisubstituted benzene derivatives, and serve by their formation to determine whether a given compound is o-, m-, or p-.

Phthalic Acid—**Benzene-o-dicarboxylic acid**— $C_6H_4(COOH)_{2(1,2)}$ —is obtained: (1) industrially by oxidation of naphthalene or tetrachloronaphthalene, for use in the manufacture of the phthalein dyes; (2) by oxidation of o-xylene, o-toluic acid, etc.; (3) by direct union of carbon monoxid with salicylic acid: $C_6H_4.OH.COOH + CO = C_6H_4(COOH)_2$; or with resorcinol: $C_6H_4(OH)_2 + 2CO = C_6H_4(COOH)_2$.

Phthalic acid crystallizes in prisms, sparingly soluble in cold water, readily soluble in hot water, alcohol, and ether, fuses at 213° ($415.4^\circ F.$). Heated with CaH_2O_2 , it is decomposed into benzene and CO_2 . Nascent hydrogen converts it into **hydrophthalic acids** (p. 492). It is the only phthalic acid which yields an anhydrid.

Isophthalic Acid—**Benzene-m-dicarboxylic acid**— $C_6H_4(COOH)_{2(3,5)}$ —is formed by oxidation of m-xylene, m-toluic acid, and other m-benzene bisubstituted derivatives. It crystallizes in fine needles, sparingly soluble in water, soluble in alcohol, fuses and sublimes above 300° ($572^\circ F.$).

Terephthalic Acid—**Benzene-p-dicarboxylic acid**— $C_6H_4(COOH)_{2(1,4)}$ —is formed by oxidation of p-xylene, p-toluic acid, and other p-benzene bisubstituted derivatives. It is insoluble in water, alcohol, and ether, and sublimes without melting.

UNSATURATED AROMATIC CARBOXYLIC ACIDS.

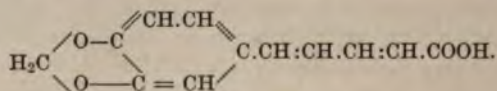
Phenyl-olefin carboxylic Acids—In some of these acids the carboxyl is attached to the benzene ring, as in **o-vinyl-benzoic acid**, $COOH.C_6H_4.(CH:CH_2)_{(o)}$. In those best known the carboxyl is in the lateral chain. They are obtained by oxidation of the corresponding alcohols or aldehydes (pp. 453, 454).

Phenyl-acrylic Acids—Two are known: **Atropic acid**, α **Phenyl-acrylic acid**, $C_6H_5.C \begin{smallmatrix} \nearrow COOH \\ \searrow CH_2 \end{smallmatrix}$, a product of decomposition of **tropic acid** (p. 463); and **cinnamic acid**, β **phenyl-acrylic acid**, $C_6H_5.CH:CH.COOH$, which exists in several balsams and resins, and is produced in the decomposition of certain alkaloids. It is also formed from benzoic aldehyde by the action of acetyl chlorid: $CH_3.CO.Cl +$

$C_6H_5.CHO = C_6H_5.CH:CH.COOH + HCl$; or, with the intermediate formation of phenyl- β -oxypropionic acid, by the action of sodium acetate in presence of acetic anhydrid: $C_6H_5.CHO + CH_3.COONa = C_6H_5.CHOH.CH_2.COONa$, and $C_6H_5.CHOH.CH_2.COONa = C_6H_5.CH:CH.COONa + H_2O$. It crystallizes in prisms, fuses at 133° ($271.4^\circ F.$), sparingly soluble in cold water, readily soluble in hot water. Oxidizing agents convert it into benzoic aldehyde and benzoic acid. It combines with hydrogen to form hydrocinnamic, or β phenyl-propionic acid, $C_6H_5.CH_2.CH_2.COOH$. Nitric acid converts it into a mixture of *o*- and *p*-nitro-cinnamic acids, the former of which is the starting point in a synthesis of indigo.

On heating with H_2O or HCl , atropic acid is converted into two polymeric isatropic acids, or diatropic acids, $(C_9H_8O_2)_2$.

Piperic Acid, obtained by decomposition of piperin by heating with alcoholic KHO , is 3-4-Methylene-dioxy-cinnamenyl-acrylic acid:



Phenyl-propionic acid $= C_6H_5.C:C.COOH$ —is a phenyl-acetylene carboxylic acid, produced by the action of carbon dioxid upon phenyl-acetylene: $C_6H_5.C:CH + CO_2 = C_6H_5.C:C.COOH$. Its *o*-nitro derivative forms isatin (p. 541) when boiled with alkalis.

PHENOL CARBOXYLIC ACIDS AND THEIR ESTERS.

These compounds have both hydroxyl and carboxyl attached to the benzene ring. They have the functions of phenol and of acid. They are formed: (1) by fusing the sulfobenzoic acids with alkalis: $C_6H_4(COOH)SO_3H + KHO = SO_3HK + C_6H_4(COOH)(OH)$, (p. 444). Also similarly from the haloid acids: $C_6H_4.Br.COOH + KHO = C_6H_4.OH.COOH + KBr$; (2) by fusion of the homologues of phenol with caustic potash, the methyl of the hydrocarbon lateral chain is oxidized to carboxyl; (3) by oxidation of the phenol-aldehydes by fusion with caustic alkalis; (4) by saponification of their esters, produced by oxidizing the sulfuric or phosphoric esters of the homologues of phenol; (5) by heating the phenols with carbon tetrachlorid and caustic potash: $C_6H_5.OH + CCl_4 + 4KHO = C_6H_4.OH.COOH + 2H_2O + 4KCl$; (6) by the action of carbon dioxid upon the sodium phenates: $2C_6H_5.O.Na + CO_2 = C_6H_4.O.Na.COONa + C_6H_5.OH$.

Di-, tri-, and tetra-carboxylic oxyacids are known. But the best known of the oxyacids are monocarboxylic, and monooxy-, dioxy-, and trioxy-, corresponding to the phenols of like hydroxyl content.

MONOXY-MONOCARBOXYLIC ACIDS.

Oxybenzoic Acids— $C_6H_4.OH.CO_2H$.—Of the three isomeric acids the meta-, f. p. 200° (392° F.), and the para-, f. p. 210° (410° F.), acids are obtained by the action of KHO on the corresponding bromobenzoic acids.

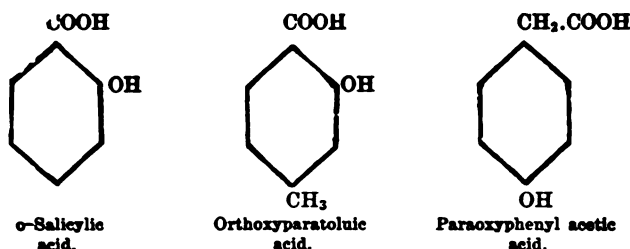
Salicylic Acid—*o*-Oxybenzoic Acid—f. p. 155° (311° F.), occurs free, accompanied by salicylic aldehyde (p. 454), in *Spiraea ulmaria* and, as its methylic ester, in oil of wintergreen. It is also formed by decomposition of salicin, coumarin or indigo. It is produced synthetically by the above reactions and, industrially, by heating sodium phenate in a current of carbon dioxid. The reaction is not $C_6H_5.ONa + CO_2 = C_6H_4.OH.COONa$, but $2C_6H_5.ONa + CO_2 = C_6H_5.OH + C_6H_4.ONa.COONa$.

Salicylic acid crystallizes in prisms or needles, sparingly soluble in cold water, readily soluble in hot water, alcohol and ether, sweet and acid in taste. When heated, it distils in part unchanged, while a part loses oxygen and yields salol and xanthone, $C_{13}H_{10}O_2$; or salol, carbon dioxid and water (see below). With Cl and Br it forms products of substitution. With fuming HNO_3 it forms a nitro-acid and, finally, picric acid. With ferric chlorid it gives a fine violet color. Nascent hydrogen causes rupture of the ring, with formation of pimelic acid (p. 338) as a final product. Salicylic acid and its salts and esters are used as antiseptics and as antirheumatics.

Phenyl Salicylate—**Salol**— $C_6H_4.OH.CO_2(C_6H_5)$ —is formed by heating salicylic acid to 220° (428° F.): $2C_6H_4.OH.CO_2H = C_6H_4.OH.CO_2(C_6H_5) + CO_2 + H_2O$; also by the action of $POCl_3$ on a mixture of salicylic acid and phenol. It is a white, crystalline powder, faintly aromatic in taste and odor, almost insoluble in water, soluble in alcohol, ether and benzene, fuses at 43° (110° F.). It is not decomposed by weak acids, but is saponified by alkalies to form salicylic acid and phenol; hence it passes unchanged through the stomach to be decomposed in the intestine: $C_6H_4.OH.CO_2(C_6H_5) + H_2O = C_6H_4.OH.CO_2H + C_6H_5.OH$.

Acetol Salicylate—**Salacetol**— $C_6H_4.OH.CO_2(CH_2.CO.CH_3)$ —the ester of the keto-alcohol, acetol (p. 308), is formed by the action of monochloroacetone on sodium salicylate. It crystallizes in plates, sparingly soluble in water, readily soluble in alcohol, fusible at 71° (159.8° F.). It is saponified by alkalies with formation of acetol and salicylic acid, and is hence substituted for salol as a medicine when the formation of phenol is undesirable. Like acetol and its other esters, it reduces Fehling's solution.

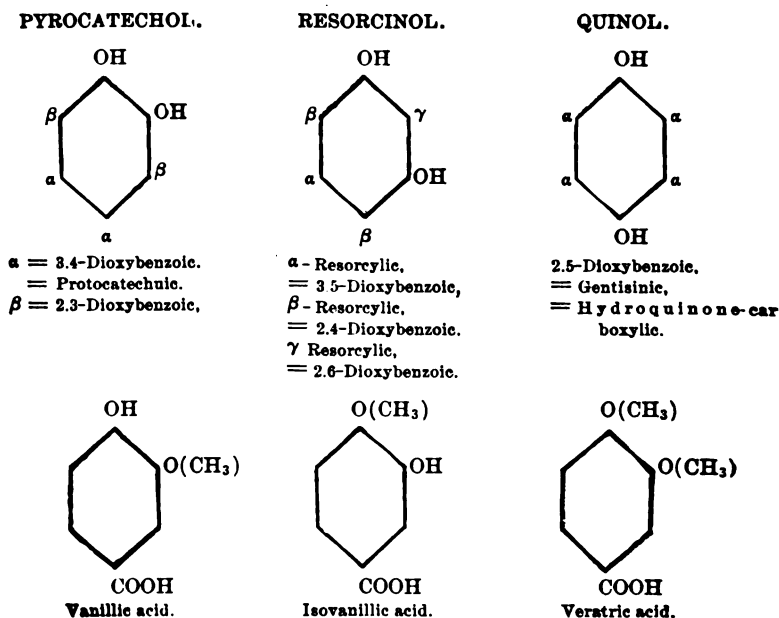
The superior homologues of the salicylic acids are either alkyl substituted derivatives of the oxybenzoic acids or oxyphenyl fatty acids:



Paraoxyphenylacetic acid and **paraoxyphenylpropionic acid**, $\text{C}_6\text{H}_4(\text{OH})_{(1)}(\text{CH}_2.\text{CH}_2.\text{COOH})_{(1)}$, the latter also called **hydroparacoumaric acid**, exist in the urine in "alkaptonuria," accompanied by **paraoxyphenylglycollic acid**, $\text{C}_6\text{H}_4(\text{OH})_{(1)}(\text{CHOH}.\text{COOH})_{(1)}$, and the dioxycarboxylic acids mentioned below. They are products of decomposition of protein material.

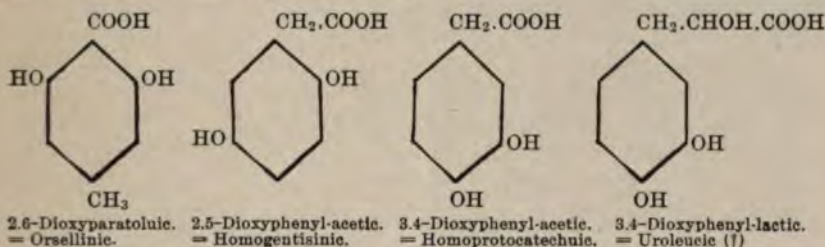
DI- AND TRIOXYMONOCARBOXYLIC ACIDS.

Dioxy-carboxylic Acids.—The six isomeres corresponding to the three diphenols are known, as well as numerous alkyl derivatives, such as vanillic, isovanillic and veratric acids, which are derived from protocatechuic acid. The relations of these acids are shown by the following formulæ:



Protocatechuic Acid—3,4-Dioxybenzoic Acid— $C_6H_3(COOH)_{(1)}(OH)_{2(3,4)}$ —exists in the fruit of the star-anise, and is produced from many resins by fusion with KHO. It is formed by fusion of dibromobenzoic acid, and other similar derivatives, with KHO.

The superior homologues of dioxy-carboxylic acids are either dioxytoluic acids, etc., such as orsellinic acid, or dioxy-phenyl fatty acids, such as homogentisinic acid:



Homogentisinic acid, or glycosuric acid, exists in the urine in "alkaptonuria," probably accompanied by homoprotocatechuic and uroleucic acids, as well as by the monoxy-monocarboxylic acids mentioned above.

Trioxycarboxylic Acids.—Three of the six possible acids are known, two derived from pyrogallol, one from phloroglucin (p. 449).

Gallic Acid— $C_6H_2(COOH)_{(1)}(OH)_{3(3,4,5)}$ —exists in nature in certain leaves, seeds and fruits. It is best obtained from nut-galls, which contain its glucosid, gallo-tannic acid. It is formed when bromoprotocatechuic acid is fused with caustic potash. It crystallizes in long, silky needles with 1Aq, odorless, acidulous in taste, sparingly soluble in cold water, very soluble in hot water and in alcohol. Its solutions are acid. When heated to $210-215^\circ$ it yields CO_2 and pyrogallol (p. 450). Its solutions reduce the salts of silver and of gold; they do not precipitate gelatin nor the salts of the alkaloids, as does tannin; and they give a blue-black precipitate with Fe_2Cl_6 .

Tannins—Tannic Acids—are substances of vegetable origin, principally derived from leaves, barks and seeds. They are amorphous, soluble in water, astringent, capable of precipitating albumin, of forming imputrescible compounds with the gelatinoids (leather), and give green or blue colors with the ferric salts.

Pure tannic acid has been obtained by removal of water from gallic acid: $2C_7H_6O_5 = C_{14}H_{10}O_9 + H_2O$; it is, therefore, digallic acid. It exists in gall-nuts, excrescences produced upon oak trees by the punctures of certain insects (gallo-tannic acid). It is colorless, amorphous, odorless, very soluble in water, less so in alcohol, almost insoluble in ether. It forms a dark-blue liquid (ink) with solutions of ferric salts or, after exposure to air, with ferrous salts.

Caffetannic Acid, $C_{30}H_{18}O_{16}$, exists in saline combination in coffee and Paraguay tea. It colors the ferric salts green, precipitates the salts of quinin and cinchonin, but not tartar emetic or gelatin, as tannic acid does. It yields **caffeic acid**, or **3-4-dioxycinnamic acid**, $C_9H_8O_4$, on decomposition. **Cachoutannic acid**, obtained from catechu, is soluble in water, alcohol and ether. It precipitates gelatin, but not tartar emetic, and colors ferric salts grayish-green. **Morintannic acid**, or **maclurin**, $C_{13}H_{10}O_6$, is a yellow, crystalline substance, obtained from fustic. It is more soluble in alcohol than in water. Its solutions precipitate greenish-black with ferric salts, yellow with lead acetate, brown with tartar emetic and yellowish-brown with cupric sulfate. **Quercitannic acid**, $C_{19}H_{16}O_{10}$, is the tannin of oak bark. It is a red powder, sparingly soluble in water, which forms a violet-red precipitate with ferric salts. **Quinotannic acid** exists in cinchona barks, in combination with the alkaloids. It is light yellow, soluble in water, alcohol and ether, astringent, but not bitter in taste. It is colored green by ferric salts. Dilute H_2SO_4 decomposes it with formation of **quina red**, an amorphous substance, which yields protocatechuic and acetic acids on further decomposition.

ALCOHOL-, ALDEHYDE-, AND KETONE-CARBOXYLIC AROMATIC ACIDS; AND THEIR ESTERS.

The aromatic alcohol-acids are of two classes: (1) **alcohol-carboxylic acids**, in which the group CH_2OH is attached to the benzene ring, and (2) **phenyl-paraffin alcohol-acids**, which contain either (CH_2OH) ; $(CHOH)$ or (CHO) in a lateral chain.

The three **oxymethyl-benzoic acids** are the best known of these acids, and of these the **o-acid**, $C_6H_4(COOH)_{(1)}(CH_2OH)_{(2)}$, a white powder, fusible, with decomposition, at 118° ($244.4^\circ F.$), produced by the action of boiling alkalies upon

Phthalid — $C_6H_4 \begin{smallmatrix} \diagup CO^{(1)} \\ \diagdown CH_2^{(2)} \end{smallmatrix} O$ — its lactone (p. 368), which is formed by several reactions, as by the reduction of phthalic anhydrid by nascent hydrogen. Phthalid crystallizes in needles, fusible at 73° ($163.4^\circ F.$), sparingly soluble in cold water, rather soluble in hot water. Reducing agents convert it into orthotoluic acid; oxidizing agents into phthalic acid. It forms a number of substituted phthalids, among which is meconin (see also p. 504).

Meconin — **5-6-Dimethyloxyphthalid** — $(CH_3O)_{2(5,6)}C_6H_2 \begin{smallmatrix} \diagup CO^{(1)} \\ \diagdown CH_2^{(2)} \end{smallmatrix} O$ — the lactone of **meconinic acid**, and the earliest known lactone, exists in opium, and is also formed by the action of reducing agents upon narcotin. It is also formed by reduction of the corre-

sponding aldehyde-acid, **opianic acid**, $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_2\text{C}(\text{COOH})\text{CHO}$, a product of decomposition of narcotin and of hydrastin. Meconin, or **opianyl**, is a neutral, non-poisonous, crystalline substance, which gives a fine green color, changing to red after 24 hours, with H_2SO_4 .

The **phenyl-paraffin alcohol-acids** may be considered as derived from the aliphatic oxyacids (p. 338) by substitution of phenyl, C_6H_5 , or phenylene, C_6H_4 , for hydrogen in the alcohol or hydrocarbon groups. They are mono- or di-carboxylic and mono- or dioxy-, and, in the higher terms, α , β , etc.

Phenylglycollic Acid—Mandelic Acid— $\text{C}_6\text{H}_5\text{C}^*\text{HOH.COOH}$ —is the lowest term of the series, and exists in three optical isomeres. The inactive acid is formed by the action of nascent hydrogen upon benzoic aldehyde, $\text{C}_6\text{H}_5\text{CHO}$, or upon benzoyl-formic acid, $\text{C}_6\text{H}_5\text{CO.COOH}$. Oxidizing agents convert it first into benzoyl-formic acid and then into benzoic acid.

Phenyllactic Acids— α and β **phenyllactic acids**, $\text{C}_6\text{H}_5\text{COH}(\text{CH}_3)\text{COOH}$, and $\text{C}_6\text{H}_5\text{CH}_2\text{CHOH.COOH}$, and α and β **phenylhydracrylic acids**, $\text{C}_6\text{H}_5\text{C}^*\text{H}(\text{COOH})(\text{CH}_2\text{COOH})$, and $\text{C}_6\text{H}_5\text{C}^*\text{H}(\text{CH}_2\text{COOH})_2$, are known (p. 341).

α **phenyllactic acid**, or **atrolactic acid**, is formed by oxidation of α -phenylpropionic acid (p. 456); or by total synthesis through methylphenyl ketone (p. 455). This is first converted into dichlorethylbenzene by phosphorus pentachlorid: $\text{C}_6\text{H}_5\text{CO.CH}_3 + \text{PCl}_5 = \text{POCl}_3 + \text{C}_6\text{H}_5\text{CCl}_2\text{CH}_3$; which is converted into methylbenzoyl cyanhydrin by potassium cyanid: $\text{C}_6\text{H}_5\text{CCl}_2\text{CH}_3 + \text{KCN} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{COH}(\text{CH}_3)\text{CN} + \text{KCl} + \text{HCl}$, and this by cold concentrated hydrochloric acid into α -atrolactic acid: $\text{C}_6\text{H}_5\text{COH}(\text{CH}_3)\text{CN} + 2\text{H}_2\text{O} + \text{HCl} = \text{C}_6\text{H}_5\text{COH}(\text{CH}_3)\text{COOH} + \text{NH}_4\text{Cl}$. This synthesis is of interest as being a step in the total synthesis of the isomere of atrolactic acid, tropic acid, and of atropin.

α -phenylhydracrylic acid is **tropic acid**, the inactive modification of which is a product of decomposition of atropin and hyoseyamin. It is formed synthetically from atropic acid (p. 457), or from atrolactic acid. The latter is first dehydrated to atropic acid: $\text{C}_6\text{H}_5\text{COH}(\text{CH}_3)\text{COOH} = \text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{COOH})_2 + \text{H}_2\text{O}$, which is then converted into β -chlorhydratropic, or α -phenyl- β -chlorpropionic acid, and this is hydrated to tropic acid: $\text{C}_6\text{H}_5\text{CH}(\text{CH}_2\text{Cl})\text{COOH} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{CH}(\text{CH}_2\text{OH})\text{COOH} + \text{HCl}$.

The **dioxy-alcohol acids** are derived from the acids of the glyceric series (p. 342), as α **phenylglyceric acid**, $\text{CH}_2\text{OH.C}(\text{C}_6\text{H}_5)\text{OH.COOH}$.

The **dicarboxylic alcohol-acids** are either **benzyl-** or **phenyl-alcohol acids** such as **benzyl-tartronic acid**, $(\text{C}_6\text{H}_5\text{CH}_2)\text{COH}:(\text{COOH})_2$; or **phenylene oxydicarboxylic acids**, such as **carbomandelic acid**,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \diagdown \\ \text{CHOH} \cdot \text{COOH} \end{smallmatrix}$. The phenylene acids readily form **phthalid acids** (lactones) more stable than themselves, such as **phthalid-acetic acid**,
 $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \text{---} \text{O} \\ \diagdown \quad \diagup \\ \text{CH} \cdot \text{COOH} \end{smallmatrix}$.

The aromatic **aldehyde acids** contain the carboxyl and aldehyde groups attached to the benzene ring, as in **opianic acid** (above).

In the **ketone acids** the ketone group (CO)'' is necessarily in a lateral chain. In some of these acids the ketone and carboxyl groups are in different lateral chains, as in **aceto-benzoic acid**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{COOH} \\ \diagdown \\ \text{CO} \cdot \text{CH}_3 \end{smallmatrix}$, but in most of them the two groups are in the same chain, and are α , β , γ , etc., according to the removal of the CO from the COOH group. Thus **benzoyl-formic acid**, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{COOH}$, is α , and **benzoyl acetic acid**, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOH}$, is β .

Besides the above there are also known: **Phenyl-alcohol-ketone acids**, such as **benzoyl-glycollic acid**, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CHOH} \cdot \text{COOH}$; **phenyl-diketone-acids**, such as **benzoyl-pyroracemic acid**, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{COOH}$; **phenyl-ketone-dicarboxylic acids**, such as **benzoyl-malonic acid**, $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH} : (\text{COOH})_2$; and **phenylen-ketone-dicarboxylic acids**, such as **phthalonic acid**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{COOH} \\ \diagdown \quad \diagup \\ \text{COOH} \end{smallmatrix}$.

PHENYLIC ETHERS—GLUCOSIDS.

The oxids of the aromatic series, corresponding to the aliphatic ethers (p. 348), and containing two cyclic hydrocarbon groups united by an oxygen atom, properly belong among the dibenzenic compounds (p. 439), but are more conveniently considered here.

Phenyl Ether—Diphenyl Oxid — $(\text{C}_6\text{H}_5)_2\text{O}$ —is formed by heating phenol with aluminium chlorid, or with zinc chlorid: $2\text{C}_6\text{H}_5 \cdot \text{OH} = \text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O}$, and by other more circuitous methods. It crystallizes in long needles, having the odor of geranium, soluble in alcohol and in ether. Corresponding to it are a number of derivatives, formed by substitution of various univalents for the remaining phenol hydrogen.

The **mixed oxids**, containing a phenyl and an alkyl group, are the phenyl ethers or phenol esters, derived from phenol (p. 446). They are formed by heating metallic phenates with alkyl halids: $\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{K} + \text{CH}_3\text{I} = \text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{CH}_3 + \text{KI}$, as the aliphatic ethers are produced from metallic alcoholates and alkyl halids (p. 349).

Methyl-phenyl Ether—Anisol— $\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{CH}_3$ —is a colorless, thin liquid, boils at 152° (305.6° F.) without decomposition. Sulfuric acid dissolves it, with formation of methyl-phenol sulfonic acid.

Ethyl-phenyl Ether—Phenetol— $\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{C}_2\text{H}_5$ —is a colorless liquid, having an aromatic odor. It boils at 172° (341.6° F.).

GLUCOSIDS.

The name "glucosid" was first applied to certain natural products, some of which are the active constituents of medicinal plants, which, on decomposition by dilute mineral acids, yield glucose and some other substance. Subsequently, it was found that the sugars derived from some of these substances differ from glucose; some are pentoses, others hexoses; some monosaccharids, others disaccharids; some aldoses, others ketoses. On the other hand, the second product of decomposition has been of the most varied character, phenols, alphenols, alcohols, oxyphenols, monobenzenic or dibenzenic, but, in all those natural glucosids which have been investigated, always a cyclic compound, containing a phenolic or an alcoholic group. The glucosids have usually been regarded as esters of glucose, etc., since the alcoholic character of the sugars has been recognized, but, as the union of the sugar and benzenic components is through an oxygen atom, and not by replacement of the hydrogen of a carboxyl, they are more properly regarded as ethers (p. 348), formed by union of an aldose or ketose remainder with one of a phenolic or alcoholic benzenic compound, with elimination of H_2O . The constitution of the glucosids cannot, however, be considered as established, as no natural glucosid has been obtained synthetically, although the products of decomposition of some are comparatively simple compounds. It is to be supposed that the union takes place through the aldehyde group, as the glucosids do not reduce Fehling's solution and do not form osazones. They probably contain some such grouping as:

$CH_2OH.(CHOH)_3.CH \begin{array}{c} \diagup O \diagdown \\ \diagdown \diagup \end{array} CH.O.B$, in which B represents the benzenic component.

The glucosids are decomposed (hydrolyzed) by heating with dilute acids, or, at very slightly elevated temperatures, by certain enzymes, such as emulsin, which exists in almonds, myrosin, in mustard seeds, the invertin of malt, and salivary and intestinal enzymes. They are very slowly hydrolyzed by heating with water under pressure, if at all; and only a few of them are decomposed by alkalies.

The glucosids yielding pentoses on hydrolysis are more properly designated pentosids.

Phenyl Glucosid—Glucosyl phenate— $C_6H_{11}O_5.O.C_6H_5$ —is the simplest of the glucosids, and is an artificial product, formed by mixing alcoholic solutions of acetochlorhydrose (p. 368) and potassium phenate, $CHO.(CH.CO_2.CH_3)_4.CH_2Cl + C_6H_5.O.K + 4H_2O = CHO.-(CHOH)_4.CH_2.O.C_6H_5 + KCl + 4CH_3.COOH$. It forms soluble, crystalline needles, fusible at 172° , and is decomposed by emulsin into glucose and phenol.

Among the more important of the natural glucosids are the following :

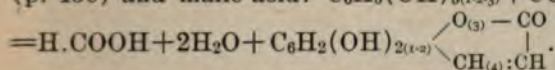
Æsculin— $C_{15}H_{16}O_8$ —which exists in the rinds of horse-chestnuts. It forms colorless crystals, sparingly soluble in water, the solutions having a brilliant blue fluorescence, even when very dilute. It forms a yellow solution with HNO_3 , which becomes deep blood-red on super-saturation with ammonia. It is decomposed by dilute mineral acids, or by emulsin, into glucose and **æsculetin**, $C_9H_6O_4$, which is probably a dioxy-derivative of coumarin (p. 539): $C_6H_2(OH)_2$ $\begin{matrix} \text{CH:CH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{CO} \end{matrix}$

Amygdalin— $C_{20}H_{27}NO_{11}$ —exists in the bitter almond, in the kernels of peach- and plum-pits, apple- and pear-seeds, and a great variety of other plants. It crystallizes in colorless prisms with 3Aq, easily soluble in water, insoluble in ether, odorless, and bitter. It is decomposed by dilute mineral acids, or by emulsin, into two molecules of glucose and one each of benzoic aldehyde and hydrocyanic acid: $C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_7O(OH)_5 + C_6H_5.CHO + CNH$. By the action of alkalies, particularly by heating with BaH_2O_2 , amygdalin yields **amygdalic acid**, $C_{20}H_{28}O_{13}$, of which amygdalin appears to be the nitril: $C_6H_7O(OH)_4.O.C_6H_7O(OH)_3.O.CH(C_6H_5)CN$, and this, on splitting off of the sugar, first forms the nitril of mandelic acid (p. 463): $C_6H_5.CHOH.CN$, the subsequent decomposition of which into $C_6H_5.CHO$ and HCN is evident. Amygdalin itself is non-poisonous, but its ready decomposition, with formation of the extremely poisonous hydrocyanic acid, is a prolific source of cyanic poisoning.

Coniferin— $C_{16}H_{22}O_8$ —is a glucosid occurring in the inner bark (cambium) of coniferous plants, and in asparagus and the sugar-beet. It crystallizes in silky, white needles, sparingly soluble in water, faintly bitter. With phenol and concentrated hydrochloric acid it assumes an intense blue color (pine-shaving reaction, p. 445). It is decomposed by emulsin into glucose and coniferyl alcohol, which is a hydroxyl-oxymethyl cinnamyl alcohol (p. 453): $CH_3-\overset{HO}{\underset{O}{\text{C}}} > C_6H_3.CH:CH.CH_2OH$. By oxidation with chromic acid it forms **glucovanillin**, $C_6H_{11}O_5.O.C_6H_3(OCH_3)CHO$, which is decomposed by emulsin into glucose and vanillin: methylprotocatechuic aldehyde (p. 454). Glucovanillin, containing an aldehyde group, forms a crystalline compound with phenylhydrazin, and an oxim. By further oxidation it forms **glucovanillic acid**, and by reduction, the corresponding alcohol.

Daphnin, $C_{15}H_{16}O_9$, occurs in the bark of *Daphne mezereum*, and other species of *Daphne*. It crystallizes in colorless prisms, bitter and astringent, sparingly soluble in water and in ether, soluble in alcohol. It is colored bluish by ferric chlorid. It is decomposed into glucose and **daphnetin**, $C_9H_6O_4$, isomeric with æsculetin (above). **Daph-**

netin has been shown to be a dioxycoumarin, having the hydroxyls in the positions 1, 2, by its synthesis by condensation of pyrogallol (p. 450) and malic acid: $C_6H_3(OH)_{3(1-2-3)} + COOH.CH_2.CHOH.COOH$



Digitalis Glucosids.—The active substance of digitalis consists, in part at least, of a glucosid, or glucosids, probably accompanied by products of decomposition, but the chemistry of these compounds requires further investigation. **Digitonin**, $C_{27}H_{44}O_{13}(?)$, is the most abundant constituent of the "amorphous digitalins," and has little or no therapeutic value. It is an amorphous, white solid, very soluble in water, which crystallizes from its alcoholic solutions. It is decomposed by dilute hydrochloric acid into **digitonein**, or **digitogenin**, $C_{15}H_{24}O_4$, glucose and galactose. **Digitalin**, $(C_5H_8O_2)_n(?)$, separates in amorphous or nodular masses from its alcoholic solution. On decomposition it yields **digitaliresin**, $C_{16}H_{22}O_2$, glucose and **digitalose**, $C_7H_{14}O_5$. It has the physiological action of digitalis upon the heart, and is the principal constituent of "Homolle's digitalin." **Digitoxin**, $C_{21}H_{32}O_7(?)$, crystallizes in fine needles, insoluble in water, soluble in hot alcohol and in chloroform. It is the most actively poisonous of the digitalis glucosids, and is the chief constituent of "Nativelle's digitalin." Digitalin gives a color-reaction which is not given by digitoxin: it forms a golden-yellow or brownish solution with concentrated H_2SO_4 , which becomes violet-red by the action of bromin-vapor.

Indican— $C_{26}H_{31}NO_{17}$ —is a glucosid occurring in the indigo plant. It is a yellow or light brown syrup, which cannot be dried without decomposition, bitter and disagreeable in taste, acid in reaction, and soluble in water, alcohol and ether. It is very prone to decomposition. Even slight heating decomposes it into leucin, **indicanin**, $C_{20}H_{23}NO_{12}$, and **indiglucin**, $C_6H_{10}O_6$. A characteristic decomposition is that by which it yields indigo-blue (p. 542) and indiglucin, along with other products: $2C_{26}H_{31}NO_{17} + 4H_2O = C_{16}H_{10}N_2O_2 + 6C_6H_{10}O_6$.

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, exists in the seeds of black mustard as its K salt, which is hydrolyzed by myrosin (p. 465) into glucose, allyl isothiocyanate (p. 432) and $KHSO_4$.

Phloridzin, $C_{21}H_{24}O_{10}$, occurs in the root-bark of apple and other fruit trees. When ingested it causes glycosuria. It is hydrolyzed by boiling with dilute acids, or even with water, into a crystalline, dextrogyrous hexose, **phlorose**, and **phlorethin**, $C_{15}H_{14}O_5$, which is further decomposed by hot alkalies into phloroglucin and **phoretic**, or **p-oxyhydratropic acid**: $C_6H_4(OH).C_2H_4.COOH$.

Salicin— $C_{13}H_{18}O_7$ —occurs in willow bark. It is a white, crystalline substance, insoluble in ether, soluble in water and in alcohol,

very bitter in taste. Concentrated H_2SO_4 colors it intensely red, the color being discharged by addition of water. It is decomposed by emulsin, by saliva, or by mineral acids into glucose and saligenin (p. 453). When taken into the economy it is converted into salicylic aldehyde and acid, which are eliminated in the urine. **Populin**, a glucosid from poplar bark, is benzoyl-salicin.

Solanin— $\text{C}_{42}\text{H}_{87}\text{NO}_{15}$ (?)—is a glucosid having basic properties, an alkaloid-glucosid, occurring in a variety of plants of the genus *Solanum*. It crystallizes in white, silky needles, acid and bitter in taste, insoluble in water, sparingly soluble in alcohol and in ether. By the action of hot dilute acids it is decomposed into glucose and a basic substance, **solanidin**.

ANHYDRIDS AND ACID HALIDS.

The aromatic acidyls form oxids, or anhydrids, and haloid compounds, corresponding to those of the aliphatic acidyls, and produced by similar methods (pp. 351, 352).

Benzoic Anhydrid— $(\text{C}_6\text{H}_5.\text{CO})_2\text{O}$ —is formed from benzoyl chlorid by several methods: as by a reaction between benzoyl chlorid and silver benzoate: $\text{C}_6\text{H}_5.\text{CO}.\text{Cl} + \text{C}_6\text{H}_5.\text{COOAg} = (\text{C}_6\text{H}_5.\text{CO})_2\text{O} + \text{AgCl}$. It is a crystalline solid, f. p. 42° , b. p. 360° .

Phthalic Anhydrid— $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ —being formed from a dicarboxylic acid, is produced from a single molecule of the acid, with elimination of H_2O . It is formed by fusing phthalic acid. It sublimes in needles; f. p. 128° (262.4°F.); sparingly soluble in cold water, soluble in hot water, with regeneration of the acid, very soluble in alcohol and in ether. It combines with phenols to form phthaleins (p. 451).

Benzoyl Chlorid— $\text{C}_6\text{H}_5.\text{CO}.\text{Cl}$ —was the first obtained of the acidyl halids. It is formed by the action of hydrochloric acid upon benzoic acid, in presence of phosphorus pentoxid: $\text{C}_6\text{H}_5.\text{COOH} + \text{HCl} = \text{C}_6\text{H}_5.\text{CO}.\text{Cl} + \text{H}_2\text{O}$; or by the action of chlorin upon benzoic aldehyde: $\text{C}_6\text{H}_5.\text{CHO} + \text{Cl}_2 = \text{HCl} + \text{C}_6\text{H}_5.\text{CO}.\text{Cl}$; or, along with acetyl chlorid, by the action of chlorin upon benzyl acetate: $\text{CH}_3.\text{CO}.\text{O}.\text{CH}_2.\text{C}_6\text{H}_5 + 2\text{Cl}_2 = \text{C}_6\text{H}_5.\text{CO}.\text{Cl} + \text{CH}_3.\text{CO}.\text{Cl} + 2\text{HCl}$. The two chlorids are separated by fractional distillation.

Benzoyl chlorid is a colorless liquid; b. p. 198° ; having a penetrating odor. With silver (or mercuric) cyanid it forms benzoic cyanid: $\text{C}_6\text{H}_5.\text{CO}.\text{Cl} + \text{AgCN} = \text{C}_6\text{H}_5.\text{CO}.\text{CN} + \text{AgCl}$. It acts readily upon the polyatomic alcohols and upon the hexoses, when shaken with their solutions in presence of caustic soda. With the hexoses pentabenzoyl compounds are formed, and crystallize out: $\text{CHO}.\text{C}_6\text{H}_5(\text{O}.\text{CO}.\text{C}_6\text{H}_5)_5 + 5\text{HCl}$. This is a reaction utilized for the isolation of hexoses and polyatomic alcohols.

A similar reaction, similarly utilized, occurs with the diamins, in which insoluble, crystalline, dibenzoyl compounds are formed: $C_2H_4(NH_2)_2 + 2C_6H_5.CO.Cl = C_2H_4(NH.CO.C_6H_5)_2 + 2HCl$.

AROMATIC SULFUR-DERIVATIVES—SULFONIC ACIDS.

Many thio-aromatic compounds are known, as thiophenol, $C_6H_5.SH$, phenyl sulfid, $(C_6H_5)_2S$, and thio-benzoic acid, $C_6H_5.COSH$. But the most important of the aromatic compounds containing sulfur are the

Sulfonic Acids (p. 372), monobasic acids containing the group SO_3H , formed by the union of the aromatic hydrocarbon, or derivative, with H_2SO_4 with elimination of OH from the acid and H from the aromatic compound, a process called "sulfonation": $C_6H_6 + H_2SO_4 = C_6H_5.SO_3H + H_2O$. The aromatic and polybenzenic sulfonic acids are formed much more readily than the corresponding aliphatic acids, and, being acid and soluble, are largely used as dyes. They are usually produced by the action of fuming H_2SO_4 upon the aromatic compound, with or without the aid of heat.

The sulfonic acids are not decomposed by boiling with alkaline solutions, but their salts, when fused with caustic alkalies, yield phenols: $C_6H_5.SO_3K + KHO = C_6H_5.OH + K_2SO_3$. Distilled with potassium cyanid they yield nitrils: $C_6H_5.SO_3K + KCN = C_6H_5.CN + K_2SO_3$. By the action of PCl_5 they are converted into their chlorids, e. g. $C_6H_5.SO_2Cl$, which may be, in turn, converted into sulfinic acids, sulfones, etc. They are easily soluble in water, and may be separated from their solutions, as sodium salts, by the addition of $NaCl$.

Benzene-monosulfonic Acid— $C_6H_5.SO_3H$ —is formed by dissolving benzene in weak fuming sulfuric acid at a slightly elevated temperature, and diluting with H_2O . It crystallizes in extremely soluble, liquescent plates with $1\frac{1}{2}$ Aq. By the action of PCl_5 upon benzene monosulfonates, benzene sulfochlorid is produced: $C_6H_5.SO_3K + PCl_5 = C_6H_5.SO_2Cl + KCl + POCl_3$. This is an oily liquid, b. p. 246° , which is a valuable reagent for amins and amido compounds (p. 380, 412).

Three benzene-disulfonic acids— $C_6H_4(SO_3H)_2$ —ortho-, meta- and para-, are known, also one benzene-trisulfonic acid— $C_6H_3(SO_3H)_3$.

Three toluene-sulfonic acids— $C_6H_4(CH_3).SO_3H$ —ortho-, meta- and para-, have been obtained. By the action of a mixture of ordinary and fuming sulfuric acids upon toluene at a temperature not exceeding 100° (212° F.), a mixture of the ortho- and para- acids is produced. When this is treated with PCl_5 , it is converted into a mixture of para- and ortho-toluene sulfonic chlorids— $C_6H_4.CH_3.SO_2Cl$. The ortho-chlorid, when acted on by dry ammonia and ammonium

carbonate, is converted into **ortho-toluene sulfamid**— $\text{C}_6\text{H}_4.\text{CH}_3.\text{SO}_2\text{NH}_2$. This product, when oxidized by potassium permanganate, is converted into **benzoyl-sulfonic imid**— $\text{C}_6\text{H}_5.\text{CO}.\text{SO}_2\text{NH}$ —or **saccharin**—an odorless, crystalline powder, having great sweetening power, its sweet taste being still detectable in a dilution of 1-50,000. Sparingly soluble in water and in ether, readily in alcohol. Its solutions are acid in reaction. When heated with Na_2CO_3 it is carbonized and gives off the odor of benzene. It is not attacked by H_2SO_4 .

Another series of sulfonic derivatives is obtained from the phenols. Among them is:

Ortho-phenol sulfonic Acid—**Sozolic acid**—**Aseptol**— $\text{C}_6\text{H}_4.(\text{OH})_{(m)}(\text{SO}_3\text{H})_{(m)}$ —which is prepared by the action of cold concentrated H_2SO_4 upon phenol. It is a reddish, syrupy liquid, soluble in H_2O in all proportions, has a faint and not disagreeable odor. It prevents fermentation and putrefaction, and is a non-poisonous, non-irritant antiseptic. The salts of this and the corresponding para- and meta-acids have been used as antiseptics and insecticides, under the name of **sulfo-carbolates**, *e. g.* **Sodii sulfo-carbolas** (U. S.).

Phenylsulfuric Acid—**Monophenyl Sulfate**— $\text{C}_6\text{H}_5.\text{O} \begin{smallmatrix} \diagup \\ \text{HO} \end{smallmatrix} \text{SO}_2$ —isomeric with the phenol monosulfonic acids, and corresponding to the acid ethyl sulfuric ester, ethylsulfuric acid (p. 359), is the acid phenyl sulfuric ester which exists in its salts in the urine, and is the type of numerous similar compounds, the "ester sulfates" (p. 728), which are formed in the economy from substances containing a phenolic hydroxyl. The potassium salt of the acid is obtained by the action of potassium pyrosulfate upon potassium phenate: $\text{S}_2\text{O}_7\text{K}_2 + \text{C}_6\text{H}_5.\text{OK} = \text{C}_6\text{H}_5.\text{O}.\text{SO}_3\text{K} + \text{SO}_4\text{K}_2$. The free acid decomposes rapidly.

NITROGEN-CONTAINING DERIVATIVES OF BENZENE.

The nitrogen derivatives of benzene are very numerous, of great variety of structure, and include among their number several substances of great industrial value.

They may be classified into five principal groups: (1) The **nitro-compounds**, derived from other benzenic compounds by substitution of NO_2 for H, and the **nitroso-compounds**, containing the nitroso group, NO; (2) The **hydroxylamin compounds**, containing the group $-\text{N} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{H} \end{smallmatrix}$, and their nitroso derivatives; (3) the **amido- and imido-compounds**, containing NH_2 and NH, the **aromatic amins**, **amids**, and **amido-acids**, and their derivatives; (4) the **azo-** and

diazo-compounds and their numerous derivatives, containing the grouping $-N=N-$; (5) the hydrazins, containing the grouping $=N-N=$, and their nitroso derivatives.

NITRO- AND NITROSO-COMPOUNDS

Nitro-benzenes.—These contain the nitro group directly attached to the carbon of the benzene ring. They are produced by the action of fuming HNO_3 , or a mixture of HNO_3 and H_2SO_4 , upon the hydrocarbons: $C_6H_6 + HNO_3 = C_6H_5.NO_2 + H_2O$. They are yellow liquids, sparingly soluble in water. Their most important property is their ready reduction, first to hydroxylamin compounds: $C_6H_5.NO_2 + 2H_2 = C_6H_5.NH.OH + H_2O$; and then to amido-compounds: $C_6H_5.NH.OH + H_2 = C_6H_5.NH_2 + H_2O$ (p. 473).

Mono-nitro-benzene—**Nitro-benzol**—**Nitro-benzene**—**Essence of Mirbane**— $C_6H_5.NO_2$ —is obtained by the moderated action of fuming HNO_3 , or of a mixture of HNO_3 and H_2SO_4 on benzene.

It is a yellow, sweet liquid, with an odor of bitter almonds; sp. gr. 1.209 at 15° ($59^\circ F.$); boils at 213° ($415.4^\circ F.$); almost insoluble in water; very soluble in alcohol and in ether. Concentrated H_2SO_4 dissolves, and, when boiling, decomposes it. Boiled with fuming HNO_3 , it is converted into **dinitro-benzenes**. It is converted into anilin by reducing agents.

It has been used in perfumery as *artificial essence of bitter almonds*; but as inhalation of its vapor, even largely diluted with air, causes headache, drowsiness, difficulty of respiration, cardiac irregularity, loss of muscular power, convulsions, and coma, its use for that purpose is to be condemned. Taken internally, it is an active poison.

Nitro-benzene may be distinguished from oil of bitter almonds (benzoic aldehyde) by H_2SO_4 , which does not color the former; and by the action of acetic acid and iron filings, which convert nitro-benzene into anilin, whose presence is detected by the reactions for that substance (p. 474).

Dinitrobenzenes.—The three dinitrobenzenes are produced by boiling the mono-nitro compound with fuming HNO_3 . The meta-compound predominates, and may be separated by fractional crystallization from alcohol. It crystallizes in plates, fusible at 90° ($194^\circ F.$), and is used in the preparation of certain dyes, and of explosives, such as **roburite**, **sicherheit**, etc. The gases resulting from such explosives are poisonous.

Nitrotoluenes.— $C_6H_4.CH_3.NO_2$ —The o- and p-compounds are produced together by nitration of toluene, and exist in the commercial nitro-benzene. They may be separated by fractional distillation, the

o- compound boiling at 218° (424.4° F.), and the p- at 230° (446° F.). By reduction they yield the corresponding toluidins, largely used in the color industry.

Nitro-phenols — Mononitro-phenols — $C_6H_4(NO_2)OH$ — (1—2), (1—3) and (1—4) are formed by the action of HNO_3 on $C_6H_5.OH$. The ortho compound (1—2) crystallizes in large yellow needles, sparingly soluble, and capable of distillation with steam. The *meta* and *para* compounds are both colorless, non-volatile, crystalline bodies. Methyl chlorid converts nitrophenols into the corresponding **nitro-anisols**, $C_6H_4.OCH_3.NO_2$, and ethyl iodid into **nitrophenetols**, $C_6H_4.OC_2H_5.NO_2$, which by reduction yield **anisidins** and **phenetidins** (p 477). Two **dinitro-phenols**, $C_6H_3.OH(NO_2)_{2(3-4)}$, and $C_6H_3.OH(NO_2)_{2(2-6)}$ are obtained by the action of strong nitric acid on phenol or on ortho- or para-mononitro phenol. They are both solid, crystalline substances, converted by further nitration into picric acid.

Trinitro-phenols— $C_6H_2(NO_2)_3OH$.—Two are known; (1) **Picric acid**—**Carbazotic acid**—**Trinitro-phenic acid**— (NO_2) in 2—4—6. It is formed by nitration of phenol, or of 1—2—4 or 1—2—6 dinitro-phenols, and also by the action of HNO_3 on indigo, silk, wool, resins, etc. It crystallizes in yellow plates or prisms, odorless, intensely bitter (*πικρὸς* = bitter); acid in reaction; sparingly soluble in water, very soluble in alcohol, ether, and benzene; it fuses at 122.5° (252.5° F.), and may, if heated with caution, be sublimed unchanged; but, if heated suddenly or in quantity, it explodes with violence. It behaves as a monobasic acid, forming salts, which are for the most part soluble, yellow, crystalline, and decomposed with explosion when heated.

Picric acid colors silk and wool yellow. It is used as a reagent for the alkaloids, with many of which it forms crystalline precipitates, as it also does with many other substances. It is sometimes added to beer and to other food articles, to communicate to them either a bitter taste or a yellow color. Its solutions give yellow, crystalline precipitates with K salts; green precipitates with ammoniacal $CuSO_4$; and an intense red color when warmed with alkaline KCN solution. It is poisonous,

Nitro-cresols— $C_6H_3.CH_3.OH.NO_2$.—The o- and p- compounds are known. They are readily converted into the corresponding dinitro compounds, $C_6H_2.CH_3.OH.(NO_2)_2$. The 2-6 dinitro compound is used as a dye in the form of its sodium salt, under the name *Victoria orange*, or *saffron surrogate*. It is poisonous.

The **nitroso-phenols** are obtained by the action of nitrous acid upon the phenols; or by the action of hydroxylammonium chlorid upon the quinones.

p-Nitroso-phenol—Quinoxim— $C_6H_4(OH)_{(1)}(NO)_{(4)}$, or $C_6H_4 \begin{smallmatrix} O \\ | \\ N.OH \end{smallmatrix}$ —(pp. 388, 409), crystallizes in needles, and explodes when heated. **Dinitroso-resorcinol**— $C_6H_2(OH)_{2(1,3)}(NO)_{2(4,6)}$ is a brown, explosive substance, used as a green dye, *solid green*.

Nitro-acids, such as *o*-, *m*-, and *p*-nitro-benzoic acids, $C_6H_4-COOH.NO_2$, etc., are known. They yield amido-acids by reduction.

HYDROXYLAMIN COMPOUNDS.

Compounds derived from hydroxylamin by substitution of phenyl or alkyl-phenyls for extra-hydroxyl hydrogen are formed as intermediate products of reduction of the nitro-benzenes (pp. 471, 483).

Phenylhydroxylamin— $C_6H_5.N \begin{smallmatrix} OH \\ | \\ H \end{smallmatrix}$ —is an intermediate product of reduction between nitro-benzene and amido-benzene: $C_6H_5.NO_2 + 2H_2 = C_6H_5.N \begin{smallmatrix} OH \\ | \\ H \end{smallmatrix} + H_2O$, and $C_6H_5.NO_2 + 3H_2 = C_6H_5.NH_2 + 2H_2O$. It is readily oxidized to nitroso-benzene and other products, and it reduces Fehling's solution and ammoniacal $AgNO_3$ solution. Mineral acids cause its intramolecular rearrangement to *p*-amido-phenol: $C_6H_5.N \begin{smallmatrix} OH \\ | \\ H \end{smallmatrix} = C_6H_4(OH)_{(1)}(NH_2)_{(4)}$. With nitrous acid it forms a nitroso derivative: $C_6H_5.N \begin{smallmatrix} OH \\ | \\ NO \end{smallmatrix}$. It is a crystalline solid; f. p. 81° ; and forms a crystalline, colorless hydrochlorid.

AMIDO-COMPOUNDS.

The **amido-benzenes** are the counterparts of the aliphatic primary monamins (p. 377). They are obtained by reduction of the corresponding nitro-compounds. The reaction is, with moderate reduction, not so simple as is expressed by the equation: $C_6H_5.NO_2 + 3H_2 = C_6H_5.NH_2 + 2H_2O$, but several important intermediate products are formed (pp. 471, 483 and above).

Anilin—Amido-benzene — Amido-benzol—Phenylamin —Kyanol —Cristallin— $C_6H_5.NH_2$ —exists in small quantity in coal-tar, and is one of the products of the destructive distillation of indigo. It is prepared by the reduction of nitro-benzene by hydrogen: $C_6H_5.(NO_2) + 3H_2 = C_6H_5(NH_2) + 2H_2O$ (see above); the hydrogen being liberated in the nascent state in contact with nitro-benzene by the action of iron filings on acetic acid.

Pure anilin is a colorless liquid; has a peculiar, aromatic odor, and an acrid, burning taste; sp. gr. 1.02 at 16° ($60.8^\circ F$); boils at 184.8° ($364.6^\circ F$.); crystallizes at -8° ($17.6^\circ F$.); soluble in 31

parts of cold water, soluble in all proportions in alcohol, ether, carbon bisulfid, etc. When exposed to air it turns brown, the color of the commercial "aniline oil," and, finally, resinifies. It is neutral in reaction. Oxidizing agents convert it into rosanilin (p. 505), from which blue, violet, red, green, or black derivatives are obtained. Cl, Br, and I act upon it violently to produce products of substitution. Concentrated H_2SO_4 converts it, according to the conditions, into sulfanilic, or *p*-amido-benzene sulfonic acid, $\text{C}_6\text{H}_4(\text{NH}_2)_{(1)}, (\text{SO}_3\text{H})_{(4)}$, or disulfanilic acid, or anilin 2-4 disulfonic acid, $\text{C}_6\text{H}_3(\text{NH}_2)_{(1)}, (\text{SO}_3\text{H})_{2(2,4)}$. With acids it unites, after the manner of ammonia, to form salts, most of which are crystallizable, soluble in water, and colorless, although by exposure to air, especially if moist, they turn red. The sulfate has been used medicinally. Potassium permanganate oxidizes it to nitro-benzene. Heated with H_2SO_4 and glycerol it produces quinolin, and substituted quinolins may be obtained by a similar reaction from substituted anilins.

Anilin itself, when taken in the liquid form or by inhalation, is an active poison, producing symptoms similar to those caused by nitro-benzene (p. 471). Its salts, if pure, seem to have but slight deleterious action.

Anilin may be recognized by the following reactions: (1) With a nitrate and H_2SO_4 : a red color; (2) cold H_2SO_4 does not color it alone; on addition of potassium dichromate, a fine blue color is produced, which, on dilution with water, passes to violet, and, if not diluted, to black. (3) With calcium hypochlorite: a violet color; (4) heated with cupric chlorate: a black color; (5) heated with mercuric chlorid: a deep crimson color; (6) in very dilute solution (1:250,000), anilin gives a rose color with chlorid of lime, followed by ammonium sulfhydrate.

Toluidins— $\text{C}_6\text{H}_4(\text{CH}_3)(\text{NH}_2)$.—Three toluidins, *o*-, *m*-, and *p*-, are known as the superior homologues of anilin. They occur in commercial anilin and play an important part in the production of anilin colors. (p. 506).

Xylidins—**Amido-xylenes**— $\text{C}_6\text{H}_3(\text{CH}_3)_2(\text{NH}_2)$.—Six compounds of this composition are known: two derived from ortho-xylene, three from meta-xylene, and one from para-xylene. Five of them exist in commercial xylidin.

The toluidins and xylidins yield products of substitution and addition similar to those of anilin.

Carbodiimids are substances having the general formula $\text{C} \begin{smallmatrix} \text{NR} \\ \text{NR} \end{smallmatrix}$, in which RR are two univalent radicals, usually belonging to the aromatic series. They are prepared from the sulfureids, by loss of the elements of carbon oxysulfid, COS, by the action of heat or of oxydants.

Derivatives of Anilin.—By the substitution of other radicals or elements for the remaining hydrogen atoms of the benzene nucleus, or for the hydrogen atoms of the amido group, NH_2 , a great number of derivatives, including many isomeres, are produced.

Chloranilins.—Three monochloranilins are known, of which two, ortho- (1—2) and meta- (1—3), are liquid. The other, para- (1—4), is solid and crystalline.

Four dichloranilins, 1—2—4, 1—2—5, 1—3—5, and 1—3—4, are known, all solid and crystalline.

Two trichloranilins, 1—2—4—6 and 1—2—4—5, are known, both solid and crystalline.

The corresponding bromanilins are also known; also a tetrabromanilin, 1—2—3—4—6, and a pentabromanilin, $\text{C}_6(\text{NH}_2)\text{Br}_5$.

Of the possible iodanilins, but four have been described: **Meta-moniodanilin** (1—3); **paramoniodanilin** (1—4); the **diiodanilin** (1—2—4); and the **triiodanilin** (1—2—4—6).

Nitranilins.—The three isomeres, ortho-, meta-, and paramononitranilins, $\text{C}_6\text{H}_4(\text{NH}_2)(\text{NO}_2)$, are formed by imperfect reduction of the dinitro-benzenes.

Two dinitranilins, $\text{C}_6\text{H}_3(\text{NH}_2)(\text{NO}_2)_2$ (1—2—4) and (1—2—6), are known.

A single trinitranilin, $\text{C}_6\text{H}_2(\text{NH}_2)(\text{NO}_2)_3$ (1—2—4—6), has been obtained by the action of alcoholic ammonia upon the ethylic or methylic ester of picric acid. It is also called **picramid**.

Anilids.—These are compounds in which one of the H atoms of the amido group has been replaced by an acid radical. Or they may also be considered as amids, whose remaining hydrogen has been more or less replaced by phenyl, C_6H_5 .

Acetanilid—Antifebrin—Phenyl-acetamid— $\text{C}_6\text{H}_5(\text{NH}.\text{CO}.\text{CH}_3)$ —is obtained either by heating together anilin and glacial acetic acid for several hours, or, better, by the action of acetyl chlorid on anilin. It forms colorless, shining, crystalline scales; fuses at 112.5° (234.5° F.), and volatilizes unchanged at 295° (563° F.). It is sparingly soluble in cold water, soluble in hot water and in alcohol.

When acetanilid is heated with an equal weight of ZnCl_2 , **flavanilin**, a colored substance having a fine green fluorescence, and soluble in warm dilute HCl , is produced.

By herbivorous animals acetanilid is eliminated as **para-amido phenol**, $\text{C}_6\text{H}_4(\text{OH})_{(v)}(\text{NH}_2)_{(4)}$; by carnivorous animals partly in that form, but mostly as **orthoxy-carbanil**, $\text{C}_6\text{H}_4(\text{N}.\text{CO})_{(v)}(\text{OH})_{(2)}$.

Acetanilid and its derivatives in the urine respond to the **indo-phenol reaction**: Boiled a few minutes with HCl , a colorless solution is formed, which, on addition of H_2O and solution of phenol

in chlorinated lime solution, assumes a turbid, dirty red color, and on addition of ammonia an indigo-blue color.

By the further substitution of a group (CH_3) in acetanilid, **methyl-acetanilid**, or **exalgine**, $\text{C}_6\text{H}_5.\text{N}(\text{CH}_3).\text{C}_2\text{H}_3\text{O}$, is produced. It is formed by the action of methyl-iodid upon sodium acetanilid, $\text{C}_6\text{H}_5.\text{NNa}.\text{C}_2\text{H}_3\text{O}$. It is a crystalline solid, sparingly soluble in H_2O , readily in dilute alcohol. Its odor is faintly aromatic.

Three **acetoluids**, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_3 \\ \text{NH}(\text{C}_2\text{H}_3\text{O})\end{smallmatrix}\right.$, ortho-, meta-, and para-, are also known. The para- and meta- compounds seem to be almost inert, while the ortho- compound is highly poisonous.

The "anilin dyes" now so extensively used, even those made from anilin, are not compounds of anilin, but are salts of bases formed from it, themselves colorless, called **rosanilins** (see p. 505).

Phenylamins — Phenylenediamins, etc. — Anilin is the simplest representative of a large class of substances. It may be considered as benzene in which H has been replaced by NH_2 , thus: $\text{C}_6\text{H}_5.\text{NH}_2$. Its superior homologues, derivable from the superior homologues of benzene, each have at least three isomeres, ortho-, meta-, and para-, according to the orientation of the groups NH_2 and $\text{C}_n\text{H}_{2n+1}$. Anilin may also be considered as ammonia in which H has been replaced by phenyl, C_6H_5 , thus being a primary monamin (see p. 377), $\text{C}_6\text{H}_5\left\{\begin{smallmatrix}\text{H} \\ \text{H}_2\end{smallmatrix}\right\}\text{N}$. The remaining two H atoms may be replaced by other radicals to form an almost infinite variety of **secondary** and **tertiary phenylamins**, precisely as in the case of the aliphatic monamins.

Possibly some of the ptomaines are phenylamins. **Mydin**, $\text{C}_8\text{H}_{11}\text{NO}$, for example, is supposed to be **oxyphenyl ethylamin**, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{OH} \\ \text{CH}_2.\text{CH}_2.\end{smallmatrix}\right.\text{NH}_2$. It is a powerful base, strongly alkaline, has an ammoniacal odor, is a strong reducing agent, is non-poisonous, and is produced after continued putrefaction at low temperatures.

Again, it is clear that, considering anilin as amido-benzene, the substitution of NH_2 is not limited to the introduction of one such group. There may be three **phenylenediamins**, $\text{C}_6\text{H}_4(\text{NH}_2)_2$, ortho-, meta-, and para-, three **triamido benzenes**, $\text{C}_6\text{H}_3(\text{NH}_2)_3$, etc.

Meta-phenylenediamin is converted into triamido azobenzene, **Bismark brown**, by nitrous acid, and is, therefore, used as a test for nitrites in water.

Phenylcarbylamin — Phenyl Isocyanid — Isobenzonitril — $\text{C}_6\text{H}_5.\text{N}:\text{C}$ — (p. 394) is formed when chloroform is heated with anilin and caustic potash in alcoholic solution (p. 279). It is a liquid, having a most persistent, disagreeable odor. Nascent hydrogen converts it into methyl anilin. Heated to 220° (428°F.), it is converted into its isomere, **benzonitril**, or **cyanobenzene**, $\text{C}_6\text{H}_5.\text{CN}$, which is a

liquid having an odor of bitter almonds; also formed by distilling potassium benzene sulfonate with potassium cyanid.

Amido-phenols — $C_6H_4 \begin{smallmatrix} \diagup \\ \text{OH} \\ \diagdown \\ \text{NH}_2 \end{smallmatrix}$ — Three are known, ortho-, meta-, and para-, obtained by the action of reducing agents upon the corresponding nitro-compounds. Their methylic ethers, $C_6H_4 \begin{smallmatrix} \diagup \\ \text{O}(\text{CH}_3) \\ \diagdown \\ \text{NH}_2 \end{smallmatrix}$ are known as **anisidins**; and their ethylic ethers, $C_6H_4 \begin{smallmatrix} \diagup \\ \text{O}(\text{C}_2\text{H}_5) \\ \diagdown \\ \text{NH}_2 \end{smallmatrix}$ as **phenetidins**.

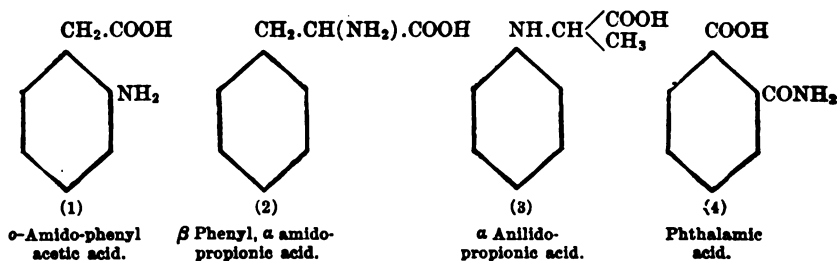
By the action of glacial acetic acid upon paraphenetidin, an aceto-derivative, **para-acetophenetidin**, $C_6H_4(\text{OC}_2\text{H}_5)_{(1)} \cdot (\text{NH} \cdot \text{C}_2\text{H}_3\text{O})_{(1)}$, is formed. It is used as an antipyretic, under the name **phenacetine**, and is a colorless, odorless, tasteless powder, sparingly soluble in H_2O , readily soluble in alcohol, fuses at 135° . Its hot aqueous solution is colored violet, changing to ruby-red, by chlorin water. The corresponding anisidin, **para-acetoanisidin**, $C_6H_4(\text{OCH}_3)_{(1)} (\text{NH} \cdot \text{C}_2\text{H}_3\text{O})_{(1)}$, **methacetine**, has also been used as a therapeutic agent. It crystallizes in white, shining, tasteless, odorless scales, fuses at 127° , sparingly soluble in H_2O , readily soluble in alcohol. It responds to the indophenol reaction (p. 475).

Aromatic acid amids are formed by methods similar to those by which the aliphatic amids are produced, and resemble them in their reactions (p. 400). Thus **benzamid**, or **benzoyl amid**, $C_6H_5 \cdot \text{CO} \cdot \text{NH}_2$, is formed by the action of benzoyl chlorid upon ammonia, $C_6H_5 \cdot \text{CO} \cdot \text{Cl} + \text{NH}_3 = \text{HCl} + C_6H_5 \cdot \text{CO} \cdot \text{NH}_2$, as a crystalline solid, fusible at 130° , or by the action of urea chlorid (p. 402) upon benzene in presence of aluminium chlorid: $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{Cl} + C_6H_6 = C_6H_5 \cdot \text{CO} \cdot \text{NH}_2 + \text{HCl}$. Two formulæ of benzamid are possible: the amid formula, $C_6H_5 \cdot \text{CO} \cdot \text{NH}_2$, and the imid formula, $C_6H_5 \cdot \text{COH} : \text{NH}$. Derivatives corresponding to each are known.

Phthalamid — $C_6H_4 \begin{smallmatrix} \diagup \\ \text{CONH}_2 \\ \diagdown \\ \text{CONH}_2 \end{smallmatrix}$, **phthalamic acid**, $C_6H_4 \begin{smallmatrix} \diagup \\ \text{COOH} \\ \diagdown \\ \text{CONH}_2 \end{smallmatrix}$, and **phthalimid**, $C_6H_4 \begin{smallmatrix} \diagup \\ \text{CO} \\ \diagdown \\ \text{CO} \end{smallmatrix} \text{NH}$ are obtained from phthalic anhydrid. The last named may be indirectly condensed, through its imid H, with the fatty acids to produce compounds which serve as starting points in syntheses of diamido fatty acids (p. 417).

The **aromatic amido-acids** greatly exceed the aliphatic (p. 411) in number and variety. They are: (1) **Amido-phenyl acids**, which may be considered either as aromatic acids, in which a ring hydrogen atom (or atoms) has been replaced by NH_2 ; or as aliphatic acids, in which amido-phenyl ($C_6H_4 \cdot \text{NH}_2$)' has replaced H in a hydrocarbon group; (2) **phenyl-amido acids**, considered either as aromatic acids, in which NH_2 replaces H in a hydrocarbon group of a lateral chain, or as amido-aliphatic acids, in which phenyl (C_6H_5)' has been substi-

tuted for H in a hydrocarbon group; (3) **anilido-acids**—aliphatic amido-acids in which phenyl has been substituted for H in NH_2 . In this class are included the anilids of the dicarboxylic acids (p. 473), e. g., **oxanilic acid**, $\text{OC} \begin{smallmatrix} \text{NH}(\text{C}_6\text{H}_5) \\ \text{COOH} \end{smallmatrix}$; (4) **amic acids** (p. 401), derived from the dicarboxylic aromatic acids by substitution of NH_2 for OH in one carboxyl group. Besides these there are amido-acids referable to 1 and 3, in which the radical benzoyl, $\text{C}_6\text{H}_5\text{.CO}$, takes the place of phenyl, C_6H_5 . The structure of these several acids is shown by the following formulæ:



Those aromatic amido-acids in which the amido group is attached to the ring do not yield monochlor-acids by treatment with NOCl , but those in which the NH_2 is in a lateral chain do, as do also the amido-acids of the acetic and oxalic series (p. 413).

Amido-phenyl Acids, of which **anthranilic**, or **o-amido-benzoic acid**, $\text{C}_6\text{H}_4(\text{COOH})_{(1)}(\text{NH}_2)_{(2)}$, is the type, are formed by reduction of the corresponding nitro-benzoic acids. Nitrous acid converts them into the corresponding oxyacids. Thus anthranilic acid yields salicylic acid. The o-acids exhibit a great tendency to the formation of lactams (p. 412), some of which are indigo derivatives, as **oxindole**,

the lactam of o-amido-phenyl acetic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}_2\text{.CO}_{(1)} \\ \diagdown \text{NH}_{(2)} \end{smallmatrix}$, and **dioxindole**, the lactam of o-amido-mandelic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH}(\text{OH})\text{CO}_{(1)} \\ \diagdown \text{NH}_{(2)} \end{smallmatrix}$, (p. 541). Isatin, a product of oxidation of indigo, is the lactam of o-amido-benzoyl-formic acid, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO.CO}_{(1)} \\ \diagdown \text{NH}_{(2)} \end{smallmatrix}$. The **amido-cinnamic acids** are closely related to quinolin (p. 543).

Phenyl-alanin (p. 414), is a **phenyl-amido acid**: **β -phenyl- α -amido-propionic acid** (formula above), which exists in certain lupines, and is a product of decomposition of the proteins. Its corresponding p-oxyphenyl derivative is

Tyrosin — **p-Oxyphenyl alanin** — $(\text{HO})_{(1)}\text{C}_6\text{H}_4\text{.CH}_2\text{.CH}(\text{NH}_2)\text{.COOH}$ —one of the earliest known products of protein decomposition.

Tyrosin is formed from proteins, particularly from casein, by the action of proteolytic enzymes, and during putrefaction, and is also formed from them by boiling with HCl or H₂SO₄, or by fusion with KHO, always accompanied by leucin (p. 414). It exists normally in the intestine, and pathologically in the urine (q. v.). It has been formed synthetically, from phenyl-acetaldehyde, C₆H₅.CH₂.CHO, by conversion into phenyl-alanin, C₆H₅.CH₂.CH(NH₂).COOH and p-amido-phenyl- α -alanin, C₆H₄(NH₂)₍₄₎.CH₂.CHNH₂.COOH. It crystallizes in silky needles, arranged in stellate bundles, very sparingly soluble in cold water, soluble in 150 parts of hot water, more soluble in the presence of acids or of alkalies, insoluble in alcohol and in ether. It unites with acids and bases to form salts. When heated it turns brown and gives off the odor of phenol; when heated to 270° (518° F.), it is decomposed into CO₂ and oxyphenylethyl-amin, C₆H₄(OH).CH₂.CH₂.NH₂, which sublimes.

With H₂SO₄, and slightly warmed, it dissolves with a transient red color; the solution, cooled, diluted, neutralized with BaCO₃, and filtered, gives a violet color with Fe₂Cl₆ (Piria's reaction). When moistened with HNO₃ and slowly evaporated, it leaves a yellow residue, which forms a deep reddish-yellow color with NaHO (Scherer's reaction). Heated with water and a few drops of Millon's reagent it gives a red liquid, and forms a red precipitate (Hofmann's reaction). Boiled with a mixture of 1 vol. formalin, 45 vols. H₂O, and 55 vols. H₂SO₄, it gives a green color (Denigès). It gives the diazo reaction.

p-Amidophenyl- α -alanin—NH₂(₄)C₆H₄.CH₂.CH(NH₂).COOH—produced by reduction of p-nitrophenyl-alanin, is both a phenyl-amide and an amido-phenyl acid.

Anilido Acids derived from the monocarboxylic acids are produced by the action of the monochlor-acids upon anilin, as the aliphatic amido-acids are obtained from ammonia (p. 412). Thus monochlor-acetic acid and anilin yield anilido-acetic acid, or phenyl glycocoll, CH₂Cl.COOH + C₆H₅.NH₂ = C₆H₅.NH.CH₂.COOH + HCl.

Hippuric Acid—Benzoyl-amido-acetic acid—Benzoyl glycocoll C₆H₅.CO.NH.CH₂.COOH—is similarly obtained from monochlor-acetic acid and benzamid: CH₂Cl.COOH + C₆H₅.CO.NH₂ = C₆H₅.CO.NH.CH₂.COOH + HCl. It is also formed by the action of benzoyl chlorid upon glycocoll in the presence of sodium hydroxid: CH₂(NH₂).COOH + C₆H₅.CO.Cl = C₆H₅.CO.CH₂.NH.COOH + HCl. Hippuric acid exists in the urine of the herbivora; and in human urine in the daily quantity of 0.29–2.84 grams, and in larger amount when benzoic acid, cinnamic acid and other aromatic substances are taken. It crystallizes in prisms, colorless, odorless, bitter, sparingly soluble in water, readily soluble in alcohol, fuses at 187° (368.6° F.). When heated with acids or alkalies it is decomposed into benzoic acid and

glycocoll. Oxidizing agents convert it into benzoic acid, benzamid and carbon dioxid. When heated alone it gives off a sublimate of benzoic acid and the odor of hydrocyanic acid. Its ferric salt is insoluble, and is formed as a brown precipitate when Fe_2Cl_6 is added to its solution. Heated with lime it forms benzene and ammonia.

Hippuric acid is the type of a class of acids derived from the aliphatic monamido and diamido acids, and from certain aromatic amido acids by substitution of cyclic acidyls for one hydrogen atom in the NH_2 groups. Some of these are synthetic products, whose formation is utilized for the separation and identification of amido acids, and are produced by the action in alkaline solution of benzoyl chlorid, benzoic anhydrid, phenyl sulfochlorid, $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{Cl}$, β -naphthalin sulfochlorid, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\text{Cl}$, 4-nitrotoluol—2-sulfonic acid, $\text{C}_6\text{H}_3\cdot\text{CH}_3\cdot\text{NO}_{2(4)}\cdot\text{SO}_3\text{H}_{(2)}$, etc., upon the amido acids.

Others, such as hippuric acid itself, occur in nature: **Ornithuric Acid—Dibenzoyl-diamido valerianic Acid**— $\text{CH}_2(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)\cdot\text{COOH}$ —occurs in the urine of hens fed with benzoic acid. It forms crystals, f. p. 182° , almost insoluble in water, acid in reaction. Its Ba salt is very soluble in water. Heated with HCl it splits to benzoic acid and benzoylornithin, which latter, on further hydrolysis, splits to benzoic acid and ornithin (p. 417).

Lysuric Acid—Dibenzoyl-diamido caproic Acid—is the corresponding acid obtained synthetically from lysin and benzoyl chlorid. It is not known to occur in nature. Its Ba salt forms crystals, almost insoluble in water, whose formation is utilized to separate lysin from arginin (p. 417).

Anilic Acids are anilido acids corresponding to the dicarboxylic acids. They may be considered as being formed by substitution of the univalent remainder of the acid for H in anilin, and therefore as anilids (p. 475); or by substitution of phenyl for H in the NH_2 group of the amic acids (pp. 402, 411). Thus **oxanilic acid**, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{COOH}$, corresponds to oxalic acid, $\text{COOH}\cdot\text{COOH}$, and to oxamic acid, $\text{CONH}_2\cdot\text{COOH}$.

Carbanilic Acid— $\text{O}:\text{C}\begin{smallmatrix} \text{OH} \\ \text{NH}\cdot\text{C}_6\text{H}_5 \end{smallmatrix}$ —the anilic acid corresponding to carbonic and carbamic acids, and isomeric with phenyl urethan (p. 402), is not known in the free state. Its esters, however, are known as phenyl urethans. A great number of **phenyl-urea** and **phenyl-guanidin** derivatives are also known.

Related to the amido acids are the **hydroxamic acids** and the **anil acids**.

Hydroxamic Acids are derivable from the imid formula of benzamid (p. 477) by substitution of OH for H in the imid group. Thus **benzhydroxamic acid**, $\text{C}_6\text{H}_5\cdot\text{C}\begin{smallmatrix} \text{NOH} \\ \text{OH} \end{smallmatrix}$, corresponds to benzamid,

$\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{NH} \\ \text{OH} \end{smallmatrix}$. Both H atoms in the OH groups are replaceable by alkyls to form esters. **Amidoxims** (p. 388) are derived from the hydroxamic acids by substitution of NH_2 for OH, e. g., **benzenylamidoxim**, $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \text{NOH} \\ \text{NH}_2 \end{smallmatrix}$.

Anil Acids are anilin derivatives of the ketone-carboxylic acids (p. 347), formed by the union of anilin and the acid, with elimination of water. Thus anilin and pyrroacemic acid yield **anil-pyrroacemic acid**: $\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{CO}\cdot\text{COOH} = \text{H}_2\text{O} + \text{C}_6\text{H}_5\text{N}:\text{C}(\text{CH}_3)\cdot\text{COOH}$.

DIAZO, DIAZOAMIDO, AND AZO COMPOUNDS.

Diazo compounds contain the group —N:N— , united by one bond to an aromatic group, and by the other to an acid radical.

Diazoamido compounds contain the group —N:N.NH— , united to two aromatic groups.

Azo compounds contain the group —N:N— , united to two aromatic hydrocarbon groups, or to one aromatic and one aliphatic hydrocarbon group.

Diazo Compounds—are derivatives of diazobenzene, $\text{C}_6\text{H}_5\text{N:NH}$, which is, however, only known in compounds in which the imid H has been replaced by acidyls or halogens, or of other cyclic compounds having the structure R.N:N.X , in which R is a cyclic hydrocarbon radical and X an acidyl or a halogen. These diazo compounds are very unstable, decomposing explosively on slight elevation of temperature or by shock. They are therefore rarely isolated in their own form of crystalline solids, but, on the other hand, their instability, or reactivity, renders their formation as intermediate products very serviceable in the formation of synthetic products, and in the manufacture of the "azo dyes," which include most of the so-called "anilin colors." Their utility in this regard depends upon the facility with which the diazo group, N:NX is displaced by other univalents, such as OH, H, CN, and halogens.

The diazo compounds are produced by the action at low temperature of HNO_2 upon the salts of the aromatic primary amines. Thus anilin chlorid yields diazobenzene chlorid: $\text{C}_6\text{H}_5\text{NH}_2\text{Cl} + \text{HNO}_2 = \text{C}_6\text{H}_5\text{N:N} + \text{NCl} + 2\text{H}_2\text{O}$. But if the temperature be allowed to rise the action proceeds further, with elimination of N and formation of a phenol: $\text{C}_6\text{H}_5\text{N:N} + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{HCl}$; the sum of the reactions upon the amin being then the same as that of HNO_2 upon the aliphatic primary amines (p. 380), i. e., the substitution of OH for NH_2 , thus $\text{C}_6\text{H}_5\text{NH}_2 + \text{HNO}_2 = \text{C}_6\text{H}_5\text{OH} + \text{N}_2 + \text{H}_2\text{O}$. This method of formation and decomposition of the diazo compounds is frequently utilized for the introduction of hydroxyl into aromatic molecules, starting either

from the hydrocarbon or intermediate forms of nitro or amido derivatives. The process is referred to as **diazotizing**. A similar decomposition is effected by simply boiling aqueous solutions of diazo compounds: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{HSO}_4 + \text{H}_2\text{O} = \text{C}_6\text{H}_5.\text{OH} + \text{N}_2 + \text{H}_2\text{SO}_4$.

The replacement of the diazo group by H, with formation of the hydrocarbon, is effected by boiling with strong alcohol, which is oxidized to aldehyde: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{HSO}_4 + \text{CH}_3.\text{CH}_2\text{OH} = \text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_2\text{SO}_4 + \text{CH}_3.\text{CHO}$. The hydracids bring about the substitution of halogen for the diazo group, with formation of a monohalid: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{HSO}_4 + \text{HI} = \text{C}_6\text{H}_5\text{I} + \text{N}_2 + \text{H}_2\text{SO}_4$. A similar decomposition is effected by Cu_2Cl_2 , and by PtCl_4 or PtBr_4 . Diazobenzene chlorid in presence of CuSO_4 is converted by KCN into diazobenzene cyanid, which then splits off N to form cyanobenzene: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{Cl} + \text{KCN} = \text{C}_6\text{H}_5.\text{N}:\text{N}.\text{CN} + \text{KCl}$, and $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{CN} = \text{C}_6\text{H}_5.\text{CN} + \text{N}_2$.

Notwithstanding the instability of the attachment of the diazo group, the diazo compounds also enter into reactions in which the N is not split off. Thus nascent hydrogen reduces the diazo salts to phenylhydrazin salts (p. 484): $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{SO}_3\text{K} + \text{H}_2 = \text{C}_6\text{H}_5.\text{HN}.\text{NH}.\text{SO}_3\text{K}$. With substances containing the grouping $-\text{CH}_2.\text{CO}-$ the diazo compounds react in alkaline solution to form hydrazones (p. 485), in which, however, the hydrazone group replaces H_2 , not O. Thus with the malonic ester: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{Cl} + \text{H}_2\text{C}:(\text{COOC}_2\text{H}_5)_2 = \text{C}_6\text{H}_5.\text{HN}.\text{N}:\text{C}:(\text{COOC}_2\text{H}_5)_2 + \text{HCl}$.

With the primary amins, whether aliphatic or aromatic, the diazo compounds form diazoamido- or disdiazaoamido compounds (below). With the phenols the diazo salts do not produce azoxy compounds (p. 483), but first diazo oxy compounds: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{HSO}_4 + \text{C}_6\text{H}_5.\text{OH} = \text{C}_6\text{H}_5.\text{N}:\text{N}.\text{O}.\text{C}_6\text{H}_5 + \text{H}_2\text{SO}_4$, which suffer atomic transposition to form oxyazo compounds: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_4.\text{OH}$, as do the diazoamido compounds (below).

Diazoamido and Disdiazaoamido Compounds.—The diazoamido compounds, containing the group $-\text{N}:\text{N}.\text{NH}-$ united to two aromatic groups, are formed by the action upon each other of diazo salts and primary or secondary amins in equal molecular proportion. Thus diazoamido benzene, $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{NH}.\text{C}_6\text{H}_5$, is formed, as a yellow, crystalline, explosive solid, insoluble in water, soluble in hot alcohol, by the action of diazobenzene nitrate, or chlorid, upon anilin: $\text{C}_6\text{H}_5.\text{N}:\text{NCl} + \text{NH}_2.\text{C}_6\text{H}_5 = \text{C}_6\text{H}_5.\text{N}:\text{N}.\text{NH}.\text{C}_6\text{H}_5 + \text{HCl}$.

The most notable property of these substances is their transformation, by intramolecular rearrangement, into the isomeric *p*-azo-amido compounds. Thus diazoamido benzene becomes *p*-azo-amido benzene, $\text{C}_6\text{H}_5.\text{N}:\text{NC}_6\text{H}_4.(\text{NH}_2)_w$. This intramolecular transposition takes place slowly in the presence of traces of anilin salts, at the ordinary temperature.

The **disdiazaoamido** compounds, containing the group $-\text{N}:\text{N}.\text{NH}-$

N:N—, are formed under the same conditions as the diazoamido compounds, except that two molecules of the diazo salt are taken for one of the amin: $2\text{C}_6\text{H}_5.\text{N}:\text{NCl} + \text{NH}_2.\text{C}_6\text{H}_5 = \text{C}_6\text{H}_5.\text{N}:\text{N}.\text{N}(\text{C}_6\text{H}_5).-\text{N}:\text{N}.\text{C}_6\text{H}_5 + 2\text{HCl}$.

Azo Compounds.—The azo compounds contain the same group, —N:N—, as the diazo compounds, but they differ from the latter in that the two valences are both satisfied by hydrocarbon groups; either both aromatic, as in **azobenzene**, $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_5$, or one aromatic and one aliphatic, as in **benzene azo-methane**, $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{CH}_3$. They are "mixed," "symmetric," and "unsymmetric," according as they contain an aromatic and an aliphatic group, or two like aromatic groups, or two unlike aromatic groups. In designating the orientation of substituted groups the —N:N— attachments are considered as occupying the (1) position in both hydrocarbon groups, and the positions of substitution in one ring are indicated by 2, 3, etc., and those in the other by 2', 3', etc.

The azo compounds are formed: (1) By moderate reduction of nitro-aromatic compounds in alkaline solution. The reaction takes place in two stages, an **azoxy** compound being first formed and then further reduced. Thus nitro-benzene forms, first **azoxybenzene**, then **azobenzene**: $2\text{C}_6\text{H}_5.\text{NO}_2 + 3\text{H}_2 = \text{C}_6\text{H}_5.\text{N} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{N}.\text{C}_6\text{H}_5 + 3\text{H}_2\text{O}$, and then $\text{C}_6\text{H}_5.\text{N} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{N}.\text{C}_6\text{H}_5 + \text{H}_2 = \text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_5 + \text{H}_2\text{O}$. The reduction readily progresses further, and always does so in acid solutions, with formation, first of a **hydrazo** product (p. 484), and finally an amido derivative (pp. 471, 473). Thus azobenzene forms, first, **hydrazobenzene**, or symmetrical diphenyl hydrazin, and then anilin: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_5 + \text{H}_2 = \text{C}_6\text{H}_5.\text{NH}.\text{NH}.\text{C}_6\text{H}_5$, and $\text{C}_6\text{H}_5.\text{NH}.\text{NH}.\text{C}_6\text{H}_5 + \text{H}_2 = 2\text{C}_6\text{H}_5.\text{NH}_2$. (2) By reduction of the azoxy compounds. (3) The amido derivatives of the azo hydrocarbons are technically manufactured by molecular rearrangement of the diazoamido compounds (p. 482), or (4) by acting upon the tertiary anilins, or upon the m-diamins, with diazo salts.

The azo compounds are much more stable than the diazo compounds. The hydrocarbons, such as **azobenzene**, $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_5$, are highly colored crystalline solids, which are not basic, and do not act as dyes. They are sparingly soluble in water, readily soluble in alcohol and in ether. Their most important derivatives are the amido-azo compounds, which are highly colored and strongly basic, crystalline solids, whose solutions have, however, no dyeing power. But they combine readily with salt-forming groups, notably to form sulfonic acids, which constitute many of the most extensively used "anilin dyes."

p-Amido-azobenzene — $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{(C}_6\text{H}_4\text{)(NH}_2\text{)}_p$ — prepared by

the methods given above, is the starting point in the manufacture of several yellow, orange, and brown "dialo dyes," and of the "inuline dyes." It forms yellow needles, fusing at 123° (253.4° F.).

HYDRAZIN COMPOUNDS.

The aromatic hydrazins are derived from diamid, $\text{H}_2\text{N.NH}_2$ (p. 152), by substitution of hydrocarbon or other aromatic radicals for one or more of the hydrogen atoms (p. 390).

Hydrazo - benzene — sym. **Diphenyl-hydrazin** — $\text{C}_6\text{H}_5.\text{NH.NH}.\text{C}_6\text{H}_5$ — is obtained by moderate reduction, as with zinc dust or sodium amalgam, of azobenzene: $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}_6\text{H}_5 + \text{H}_2 = \text{C}_6\text{H}_5.\text{NH.NH}.\text{C}_6\text{H}_5$. It forms colorless crystals, having the odor of camphor, fusible at 132° , insoluble in water, soluble in alcohol and in ether. It readily oxidizes to azobenzene. Strong reducing agents break it up into two molecules of anilin. It is not basic; but, when treated with strong acids, it suffers molecular rearrangement, with formation of **benzidin**, or $\text{p}_{(2)}\text{-diamido-diphenyl}$ (p. 502), $\text{NH}_{2(4)}.\text{C}_6\text{H}_4.\text{C}_6\text{H}_4.\text{NH}_{2(4)}$.

The **unsymmetrical hydrazins** resemble each other in their properties and methods of formation, but differ from the symmetrical compounds, notably in that, containing the —NH.NH_2 group, they are monacid bases, forming salts corresponding to those of ammonia.

Phenylhydrazin — $\text{C}_6\text{H}_5.\text{NH.NH}_2$ — is formed by reduction of the diazo salts, of the diazo-amido compounds, or of the nitroso-amins. Thus stannous chlorid and diazobenzene chlorid yield phenylhydrazin hydrochlorid: $\text{C}_6\text{H}_5.\text{N}:\text{NCl} + 2\text{SnCl}_2 + 4\text{HCl} = \text{C}_6\text{H}_5.\text{NH.NH}_3\text{Cl} + 2\text{SnCl}_4$. Zinc dust and acetic acid decompose diazoamido-benzene into phenylhydrazin and anilin: $\text{C}_6\text{H}_5.\text{N}:\text{N.NH}.\text{C}_6\text{H}_5 + 2\text{H}_2 = \text{C}_6\text{H}_5.\text{NH.NH}_2 + \text{NH}_2.\text{C}_6\text{H}_5$.

Phenylhydrazin is a yellow oil, which crystallizes at 23° (73.4° F.), and boils at 242° (467.6° F.) with partial decomposition, or at 120° (248° F.), without decomposition, under 12 mm. pressure. It reduces Fehling's solution, or when boiled with CuSO_4 it liberates nitrogen and forms benzene. Sodium displaces the imid H to form α sodium phenylhydrazin: $\text{C}_6\text{H}_5.\text{NaN.NH}_2$. The alkyl halids cause substitution of alkyls for both amid and imid H, forming α and β **phenylalkyl hydrazins**. One of the latter, β **methyl-phenylhydrazin**, $\text{C}_6\text{H}_5.\text{NH.NH}.\text{CH}_3$, is an intermediate product in the formation of antipyrin from phenylhydrazin. Heated to 200° (392° F.) with fuming HCl, phenylhydrazin is converted into **p-phenylene-diamin**: $\text{C}_6\text{H}_5.\text{NH.NH}_2 = \text{NH}_2.\text{C}_6\text{H}_4.\text{NH}_2$.

Phenyl-hydrazones and **Osazones**. — A most important action of phenylhydrazin is that with aldehydes and ketones, and with aldo-

and keto-alcohols, and aldehyde and ketone acids and their esters, in which the bivalent remainder $=N.NH.C_6H_5$ takes the place of oxygen in the aldehyde or ketone group, with the formation of **phenylhydrazones** and **osazones**, in much the same manner as the aldoxims and ketoxims are formed from the aldehydes and ketones (pp. 409, 410). The formation of these derivatives is utilized to identify the aldehydes and ketones and, notably, the aldoses and ketoses (p. 310, also "phenylhydrazin reaction").

The phenylhydrazones and osazones are formed by a variety of methods, usually by heating the aldehyde or ketone compound with phenylhydrazin hydrochlorid in presence of sodium acetate. In the formation of the **aldehydrazones** and **ketoaldehydrazones** the reaction takes place with elimination of water according to the equations: $CH_3.CH_2.CHO + H_2N.NH.C_6H_5 = CH_3.CH_2.CH:N.NH.C_6H_5 + H_2O$, and $CH_3.CO.CH_3 + H_2N.NH.C_6H_5 = CH_3.C:(N.NH.C_6H_5).CH_3 + H_2O$.

The **osazones** of the aldoses and ketoses differ from their hydrazones in that in the former two $:N.NH.C_6H_5$ groups are introduced into the sugar molecule, while the latter contain but one such group. The reaction of their formation takes place in three stages. Thus with glucose and fructose respectively (pp. 314, 315): In the first stage the hydrazone is formed: $CHO.(CHOH)_4.CH_2OH + H_2N.NH.C_6H_5 = CH(:N.NH.C_6H_5).(CHOH)_4.CH_2OH + H_2O$, and $CH_2OH.CO.(CHOH)_3.CH_2OH + H_2N.NH.C_6H_5 = CH_2OH.C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + H_2O$. In the second stage the CH_2OH group or the $CHOH$ adjoining the position of first substitution is dehydrated to CHO or CO , with formation of ammonia and anilin: $CH(:N.NH.C_6H_5).(CHOH)_4.CH_2OH + H_2N.NH.C_6H_5 = CH(:N.NH.C_6H_5).CO.(CHOH)_3.CH_2OH + NH_3 + C_6H_5.NH_2$, and $CH_2OH.C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + H_2N.NH.C_6H_5 = CHO.C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + NH_3 + C_6H_5.NH_2$. In the third stage the second $:N.NH.C_6H_5$ group replaces the O in CO or CHO . Thus, $CH(:N.NH.C_6H_5).CO.(CHOH)_3.CH_2OH + H_2N.NH.C_6H_5 = CH(:N.NH.C_6H_5).C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + H_2O$, and $CHO.C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + H_2N.NH.C_6H_5 = CH(:N.NH.C_6H_5).C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + H_2O$.

Comparison of the above formulæ of the final products from glucose and from fructose shows them to be identical; and, indeed, glucose and fructose yield one and the same osazone, called **glucosazone**. And, as glucosazone on reduction yields fructosamin: $CH(:N.NH.C_6H_5).C(:N.NH.C_6H_5).(CHOH)_3.CH_2OH + 3H_2 + H_2O = H_2N.CH_2.CO.(CHOH)_3.CH_2OH + 2C_6H_5.NH_2 + NH_3$, and this is converted into fructose by nitrous acid: $H_2N.CH_2.CO.(CHOH)_3.CH_2OH + HNO_2 = CH_2OH.CO.(CHOH)_3.CH_2OH + N_2 + H_2O$, we may convert glucose into fructose by passing through the common osazone.

The phenyl-hydrazones are also utilized in the formation of condensed heterocyclic compounds. Thus acetone phenyl hydrazone, $\text{CH}_3\text{C}(\text{N}:\text{NH}.\text{C}_6\text{H}_5)_2$ is converted into a methyl indole (p. 540), $\text{CH}_3\text{C}(\text{NH})=\text{CH}-$ C_6H_4 , by loss of NH_3 .

Acid Derivatives of Phenylhydrazin.—A great number of compounds are known, formed by the substitution of acid radicals for the amid or imid hydrogen of phenylhydrazin. These compounds bear the same relation to phenylhydrazin that the anilids bear to anilin, and some of them have been used as antipyretics, e. g., β acetophenyl-hydrazid — Hydracetin — $\text{C}_6\text{H}_5.\text{NH}.\text{NH}.\text{CO}.\text{CH}_3$ — formed as a white, crystalline, tasteless, and odorless powder, sparingly soluble in water, by the action of acetyl chlorid or of acetic anhydrid upon phenylhydrazin. It is the active ingredient of an antipyretic called pyrodin.

B. HYDROAROMATIC COMPOUNDS WITH A SINGLE NUCLEUS.

The hydroaromatic compounds may be considered as derived from the benzenic by rupture of one or more of the double linkages of the benzene ring (p. 435), by which the valence of the nucleus is changed from six to eight, ten or twelve.

HYDROCARBONS.

Hexahydrobenzenes — Cyclohexanes — Naphthenes. — These compounds, of which hexahydrobenzene, $\text{H}_2\text{C}\langle\text{CH}_2.\text{CH}_2\rangle\text{CH}_2$, is the simplest, and the parent substance of the hydroaromatic compounds, exist in Russian petroleum, in coal tar, and in "rosin-oils." They are isomeric with the olefins, from which they may be distinguished by the fact that they do not combine with bromin.

Tetrahydrobenzenes — Cyclohexenes — Naphthylenes — of which the lowest term is tetrahydrobenzene, $\text{H}_2\text{C}\langle\text{CH}_2.\text{CH}\rangle\text{CH}$, exist in rosin-oils.

Dihydrobenzenes — Cyclohexadienes — of which the first member is dihydrobenzene, $\text{HC}\langle\text{CH}.\text{CH}_2\rangle\text{CH}$, probably exist in many of the natural products called

Terpenes. — Most of the volatile, or essential oils, or essences, obtained by distillation of various plants with steam, consist of hydrocarbons having the formula $\text{C}_{10}\text{H}_{16}$, and most of the camphors and

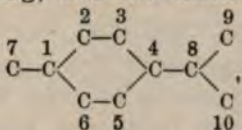
resins are alcoholic or ketonic derivatives of these hydrocarbons. A few of the essential oils, having the formula C_5H_8 , are known as **hemiterpenes**, or **olefin terpenes**, and are unsaturated aliphatic compounds (p. 425). Some of the aromatic terpenes also are polymers, having the formulæ $x(C_5H_8)$. Although the constitution of the aromatic terpenes is not completely established, they are hydroaromatic hydrocarbons of which the camphors are alcohols or ketones.

The terpenes form benzenic compounds by oxidation. With the halogens they form addition products, which not only serve for their classification, but also for their conversion into alcohol-camphors. With nitrosyl chlorid, $NOCl$, they form well-defined **nitroso-chlorids**, as **dipentene nitroso-chlorid**, $C_{10}H_{16}(NO)Cl$, which serve for their identification, and for the preparation of basic and other derivatives.

The true terpenes and their derivatives are arranged in two classes: (1) The *Terpan group*, and (2) the *Camphan group*.

The **terpan**s are capable of taking on four bromin atoms, and therefore have two double linkages. It is assumed that in them the ten carbon atoms are arranged in a hexacarbon ring, with two lateral

chains in the p- position to each other, thus:



and that two of the ten bonds are double. The hydrocarbons are, therefore, **dihydrocymenes** (p. 442). The carbon atoms are numbered as above to indicate the positions of the double linkages, which vary in the different isomeres. The positions of double linkage are marked by the Greek capital Δ , followed by the numbers of the carbon atoms from which the attachment proceeds:

Limonene— $\Delta_{(1,6)}$ **Dihydrocymene**— $CH_3.C \begin{smallmatrix} \swarrow CH & \searrow CH_2 \\ \swarrow CH_2 & \searrow CH_2 \end{smallmatrix} C^*H.C \begin{smallmatrix} \swarrow CH_2 \\ \swarrow CH_3 \end{smallmatrix}$ (probably) exists in three optical isomeres: **d-limonene**; b. p. 175° (347° F.); $[a]_D = +106.8^\circ$; a liquid having the odor of lemons, existing in many essential oils, such as those of orange, bergamot, dill, etc.: **l-limonene**; b. p. 175° (347° F.); $[a]_D = -105^\circ$; occurs in the oils of peppermint, fir and pine needles. **[d+1]-limonene**, **dipentene**, or **cinene**; b. p. 175° (347° F.); occurs in oil of wormseed, and is produced by the action of a heat of 250° – 300° upon limonenes, pinene and camphene, and therefore exists in turpentine oil produced at high temperatures, such as the Russian and Swedish. The limonenes are liquids having the odor of lemons, and combining with bromin to produce solid **tetrabromids** having the same optical action as the parent hydrocarbons.

Other terpan are: **Terpinolene**; f. p. 75° ; formed when terpin hydrate, terpineol, or cineol is heated with dilute H_2SO_4 , or by the

action of the concentrated acid on pinene. **Sylvestrene**; b. p. 176° $[a]_D = +66.32^{\circ}$; occurs in Swedish and Russian turpentine. **Terpinene**; b. p. 180° ; is formed when dipentene, terpin, phellandrene, terpineol or cineol is heated for some time with dilute alcoholic H_2SO_4 , or by the action of the concentrated acid on pinene, or by the action of formic acid on linalool (p. 427). It is not converted into other terpanes by acids, and does not yield a bromin derivative, but forms a nitroso-chlorid. **Phellandrene**; b. p. 170° ; exists in d- and l-modifications. It has the same negative qualities as terpinene. **Menthene**, $C_{10}H_{18}$, is a hydroterpan, formed by acting upon potassium phenate with menthyl chlorid; b. p. 167° .

The members of the **camphan group** are capable of taking up two bromin atoms, and are considered as probably containing a dihydrobenzene ring with a $\begin{smallmatrix} CH_3 \\ | \\ -C- \\ | \\ CH_3 \end{smallmatrix}$ group linking the p-positions internally, as in the probable formula of

Camphene — $CH_3 - C \begin{smallmatrix} \diagup CH_2 - CH_2 \diagdown \\ (CH_3.C.CH_3) \\ \diagdown CH = CH \diagup \end{smallmatrix} - CH$ — which is a solid; f. p. 43° ($109.4^{\circ} F.$); b. p. 160° ($320^{\circ} F.$); $n_D = 1.45514$ (54°); (p. 34); known in d-, l-, and [d+l] modifications. It exists in Ceylon citronella oil, and is produced by the action of dehydrating agents upon its alcohol, Borneo-camphor (p. 491). It forms a dibromid.

Pinene — $C_{10}H_{16}$ — is the principle constituent of oil, or essence of turpentine, and exists also in many other essential oils. It is a colorless liquid; b. p. 155° ; sp. gr. 0.858 (20°); $n_D = 1.46553$ (21°). It exists in three optical isomeres: **d-pinene**; $[a]_D = 17^{\circ}$; predominates in American oil of turpentine; **l-pinene**; $[a]_D = -40.3^{\circ}$; in the French oil. Pinene combines with bromin to form a **dibromid**; it, therefore, contains one double linkage. When dry HCl gas is passed through pinene, well cooled, a white, crystalline substance, fusing at 125° , and having the odor of camphor, separates. This is **d-pinene hydrochlorid**, $C_{10}H_{17}Cl$, or "artificial camphor."

Turpentine is a yellowish-white, semi-solid substance, having a balsamic odor, which exudes from incisions in the bark of *Pinus palustris*, *P. taeda*, and other *Coniferæ*, and which may be taken as the type of a number of other similar products. These substances, when distilled with steam, yield two products, one a solid, yellow or brown residue, a **stearoptene**, such as **rosin** or **colophany**; the other a volatile, oily liquid, an **eleoptene**, such as **oil**, or **essence, of turpentine**. Oil of turpentine is insoluble in water, mixes with alcohol and with ether, and dissolves phosphorus, sulfur and caoutchouc. When exposed to the air it is oxidized to gummy, aldehydal products, which finally harden, hence its use as a drier in the manufacture of paints and varnishes. On contact with HNO_3 , its oxidation is

so violent as to cause ignition. H_2SO_4 also acts upon it energetically, with formation of a number of polymeres.

Hydroterpenes are naphthenes (p. 486) obtained by decomposition of certain natural alcohol-camphors. Thus **hexahydrocymene**, $\text{H}_3\text{C}.\text{CH} \begin{smallmatrix} \text{CH}_2.\text{CH}_2 \\ \text{CH}_2.\text{CH}_2 \end{smallmatrix} \text{CH}.\text{CH} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_3 \end{smallmatrix}$, is derived from menthol (p. 490).

HYDROAROMATIC ALCOHOLS.

The **hydroaromatic alcohols** are, for the most part, "ring alcohols," and contain either CHOH or COH , as a part of the ring, although in some, as in some of the terpan alcohols (p. 490), the alcoholic group, which may then also be CH_2OH , is contained in the lateral chain. These alcohols may be obtained by reduction of the corresponding ketones (p. 491), or of other aromatic or hydroaromatic compounds. Several of them, such as quercite, inosite and some of the camphors, are natural products.

Quinite — $\text{HOHC} \begin{smallmatrix} \text{CH}_2.\text{CH}_2 \\ \text{CH}_2.\text{CH}_2 \end{smallmatrix} \text{CHOH}$ — and **phloroglucite** — $\text{HOHC} \begin{smallmatrix} \text{CH}_2.\text{CHOH} \\ \text{CH}_2.\text{CHOH} \end{smallmatrix} \text{CH}_2$ — are reduction products of the phenols, **quinol**, $\text{HOC} \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix} \text{COH}$, and **phloroglucin**, $\text{HOC} \begin{smallmatrix} \text{CH}:\text{COH} \\ \text{CH}:\text{COH} \end{smallmatrix} \text{CH}$ respectively (p. 449).

Quercite — $\text{H}_2\text{C} \begin{smallmatrix} \text{CHOH}.\text{CHOH} \\ \text{CHOH}.\text{CHOH} \end{smallmatrix} \text{CHOH}$ — a pentatomic alcohol, obtained from acorns. It is a sugar-like substance, but is not affected by alkalies, does not ferment, and does not reduce Fehling's solution. F. p. 235° ; $[\alpha]_D = +24.16^\circ$.

Inosite — $\text{C}_6\text{H}_5(\text{OH})_6$ — metameric, though not related, to the glucoses, is a hexatomic alcohol, which exists in three optical modifications. The inactive modification exists in the liquid of muscular tissue, in the lungs, kidneys, liver, spleen, brain and blood; in traces in normal urine, and increased in Bright's disease, in diabetes, and after the use of drastics in uræmia; in the contents of hydatid cysts; in beans and peas, and in certain other seeds and leaves. It crystallizes in needles, usually arranged in cauliflower-like masses, has a sweet taste, is readily soluble in water, sparingly soluble in alcohol, insoluble in absolute alcohol and in ether. It does not ferment, is not colored by alkalies, and does not reduce Fehling's solution. When heated to 170° (338°F.) with HI , it is decomposed into phenol, diiodophenol and benzene. When treated with HNO_3 , evaporated to near dryness, the residue moistened with NH_4HO and CaCl_2 , and again evaporated, a rose-red residue is left (Scherer's reaction). Mercuric nitrate produces in solutions of inosite a yellow precipitate, which, on cautious heating, turns red. The color disappears on cooling and reappears on heating (Gallois' reaction).

Dambonite, a supposed glucosid (p. 465) obtained from an African caoutchouc, is the dimethyl ether of i-inosite (dambose).

The **terpan alcohols** are derivatives of **hexahydrocymene**, or **menthan** (p. 489), $\text{H}_3\text{C} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$, or $\text{C}_{10}\text{H}_{20}$; or of **menthene**, $\text{C}_{10}\text{H}_{18}$; or of **menthadiene**, $\text{C}_{10}\text{H}_{16}$; differing from menthan by the introduction of one and two double bonds respectively. They are monacid, diacid, etc., according to the number of hydroxyls substituted for hydrogen. Among them are menthol and terpin and its hydrate.

Menthol — Oxyhexahydrocymene — $\text{H}_3\text{C} \cdot \text{CH} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}(\text{OH}) \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$ — is a monacid menthan alcohol. It is the chief constituent of oil of peppermint. It crystallizes in prisms, fusible at 42° (107.6° F.), sparingly soluble in water, readily soluble in alcohol, ether and carbon bisulfid, and in acids. Corresponding to it are a series of menthyl esters.

Terpins.—There are two diacid **menthan alcohols**, in which the hydroxyls occupy the 1,8 positions (p. 487). The formula of **cis-terpin**, the parent substance of terpin hydrate and of cineol, is now considered as being $\begin{smallmatrix} \text{H}_3\text{C} & & \text{CH}_2 \cdot \text{CH}_2 \\ & \diagdown & \diagup \\ & \text{C} & \\ & \diagup & \diagdown \\ \text{HO} & & \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \begin{smallmatrix} & \text{H} \\ & \diagdown \\ & \text{C} \\ & \diagup \\ & \text{OH} \\ & \text{C} = (\text{CH}_3)_2 \end{smallmatrix}$, while in **trans-terpin** the positions of the CH_3 and OH attached to C(1) are reversed. Cis-terpin is obtained by dehydration of terpin hydrate, and also from [d+1]-limonene dihydrochlorid (p. 487). It is crystalline, fuses at 104° (219.2° F.), and boils at 258° (496.4° F.). It absorbs water eagerly to form terpin hydrate. Gaseous HCl , or PCl_3 , converts it into [d+1]-limonene hydrochlorid.

Terpin Hydrate — $\text{C}_{10}\text{H}_{18}(\text{OH})_2 + \text{H}_2\text{O}$ — is formed when oil of turpentine remains long in contact with water, more rapidly in presence of alcohol and dilute HNO_3 ; also, similarly, from pinene and from limonene. It forms rhombic crystals, fusible at 117° (242.6° F.), with loss of H_2O and conversion, slowly, into terpin. It is easily soluble in alcohol, sparingly soluble in water, chloroform and ether. It is used as an expectorant.

Cineol — Eucalyptol — $\text{C}_{10}\text{H}_{18}(\text{OH})_2$ — another diacid menthan alcohol, is obtained from the leaves of *Eucalyptus globulus*, and also exists in wormseed oil (*Oleum cinæ*) and in other volatile oils. It is a colorless oil, having a camphor-like odor; sp. gr. 0.93 at 15° ; b. p. 176° ; $n_D = 1.4559$; soluble in alcohol, sparingly soluble in water. Dry HCl gas passed through its petroleum ether solution separates white scales of **eucalypteol**, $\text{C}_{10}\text{H}_{16} \cdot 2\text{HCl}$, which is decomposed by water with regeneration of cineol.

Terpineols are monacid **menthene alcohols**. The Δ_1 , $(\text{OH})_{(8)}$ ter-

pineol is formed by removal of $2\text{H}_2\text{O}$ from terpin hydrate. It is a solid; f. p. 35° (95°F.). When boiled with dilute acids it forms carvacrol (p. 447), and the ketone, carvone (below). It forms dipentene when heated with KHSO_4 .

Borneol—Camphol—Borneo Camphor— $\text{C}_{10}\text{H}_{18}\text{O}$ —a monacid alcohol, is the best known of the camphan alcohols. It exists in three optical modifications; the *d*-borneol being the one usually met with, and obtained from *Dryobalanops camphora*. The *d*- and *l*-modifications are both formed by hydrogenation of laurel camphor. It forms small, friable crystals; has an odor recalling those of laurel camphor and of pepper, and a hot taste; is insoluble in water, readily soluble in alcohol, ether, and acetic acid; fuses at 203° (397.4°F.); boils at 212° (413.6°F.). It is oxidized to laurel camphor by HNO_3 . Heated with KHSO_4 , it is decomposed into camphene (p. 488) and H_2O .

HYDROAROMATIC KETONES AND ACIDS.

The hydroaromatic ketones are "ring ketones," the CO group forming a part of the ring. They are formed: (1) by reduction of the corresponding aromatic phenols; (2) by oxidation of the secondary ring-alcohols; (3) by condensation of the esters of the aliphatic ketone acids (p. 347), or of the ketones. The **terpan** and **camphan ketones** exist in nature. The ketones form ketoxims with hydroxylamin (p. 409), and hydrazones with phenyl hydrazin (p. 485), which serve for their identification.

Pimelin-ketone— $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2.\text{CH}_2 \\ \text{CH}_2.\text{CH}_2\end{smallmatrix}\rangle\text{CO}$ —is the simplest of the hydroaromatic ketones. It is an oil, having the odor of peppermint; b. p. 155° ; formed by electrolytic reduction of phenol; by oxidation of **hexahydrophenol**, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2.\text{CH}_2 \\ \text{CH}_2.\text{CH}_2\end{smallmatrix}\rangle\text{CHOH}$; or by distillation of calcium pimelate, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2.\text{CH}_2.\text{CO}_2 \\ \text{CH}_2.\text{CH}_2.\text{CO}_2\end{smallmatrix}\rangle\text{Ca}$ (p. 338). Its oxim fuses at 88° .

The **terpan ketones**, or **ketohydro-p-cymenes**, are formed by oxidation of the corresponding secondary alcohols (p. 489).

Menthone— $\text{C}_{10}\text{H}_{18}\text{O}$ —(CO-3)—is a **ketomenthan**, existing in oil of peppermint. It is known in two optical isomeres: **l-menthone** is formed by oxidizing menthol, and is converted into **d-menthone** by contact with H_2SO_4 . B. p. 206° ; $[\alpha]_D = -28^\circ$ and $+28^\circ$. **l-Menthoxim** fuses at 59° .

Thujone—Tanacetone—and **Pulegone**— $\text{C}_{10}\text{H}_{16}\text{O}$, are **ketomenthenes**, the former, b. p. 200° , existing in tansy and thuja oils; the latter, b. p. 221° , in "polei-oils."

Carvone—Carvol— $\text{C}_{10}\text{H}_{14}\text{O}$ —is a **ketomenthadiene**, known in three optical isomeres, which boil at 225° . **d-Carvol** exists in cumin

and dill oils; $[a]_D = +62^\circ$. Heated with KHO, it is converted into its isomere carvacrol (p. 447). The three carvoxims are formed either by the action of hydroxylamin upon the corresponding carvones, or by the action of boiling KHO upon the three limonene nitrosochlorides (p. 487).

d-Camphor—**Common camphor**—**Laurel camphor**—**Japan camphor**— $C_{10}H_{16}O$ —is the most important of the camphan ketones. It is obtained from the camphor tree (*Laurus camphora*), and is formed artificially by oxidation of borneol or of camphene. It forms translucent, friable crystals; hot and bitter in taste, aromatic; sparingly soluble in water, quite soluble in acetic acid, methylic and ethylic alcohols, and the oils; f. p. 175° (347° F.); b. p. 204° (399.2° F.); sp. gr. 0.985; sublimes at all temperatures; $[a]_D = +44.22$.

It ignites readily, and burns with a luminous flame. Cold HNO_3 dissolves it, and H_2O precipitates it unchanged from the solution. Hot HNO_3 , or potassium permanganate, oxidizes it to d-camphoric acid. Distilled with P_2O_5 it yields cymene, $C_{10}H_{14}$. Reducing agents convert it into borneol. Heated with iodine, it is converted into carvacrol (p. 447). Bromine unites with it to form ruby-red crystals of an unstable compound, $C_{10}H_{14}OBr_2$, which, when heated, fuse and give off HBr, leaving an amber-colored residue, which, on recrystallization from boiling alcohol, leaves long, hard, rectangular crystals of **monobromo-camphor**, $C_{10}H_{15}OBr$; f. p. 76° ; soluble in alcohol and in ether.

l-Camphor is obtained from the oil of *Matricaria postlanium*; $[a]_D = -44.22^\circ$. **[d+l]-Camphor** exists in the essential oils of rosemary, sage, lavender and origanum, or is formed by mixing d- and l- camphors, or by oxidation of [d+l]-borneol, or of [d+l]-camphene. F. p. 179° .

Hydroaromatic Carboxylic Acids.—A great number of these acids are known, some pure acids, others oxy- or ketonic acids, containing from one to six carboxyl groups, and hexahydro-, tetrahydro- and dihydro-. The most important are:

Quinic Acid—**Hexahydro-tetraoxybenzoic Acid**— $C_6H_7(OH)_4 \cdot COOH$ —which exists, combined with the alkaloids, in cinchona barks, also in coffee beans and in other plants. It forms hard, transparent prisms, soluble in water and in alcohol; fuses at 160° ; laevogyrous. On distillation, it yields phenol, hydroquinol, benzoic acid and salicylic aldehyde. Hydriodic acid reduces it to benzoic acid.

Terebic Acid— $C_7H_{10}O_4$ —f. p. 175° ; and **Terpenylic Acid**— $C_8H_{12}O_4$ —f. p. 90° , are oxidation products of oil of turpentine, obtained, the former with HNO_3 , the latter with chromic acid mixture.

Camphoric Acids— $C_{10}H_{14}(COOH)_2$.—The d-, l-, and [d+l]-acids are known. **d-Camphoric acid** is produced by oxidizing common

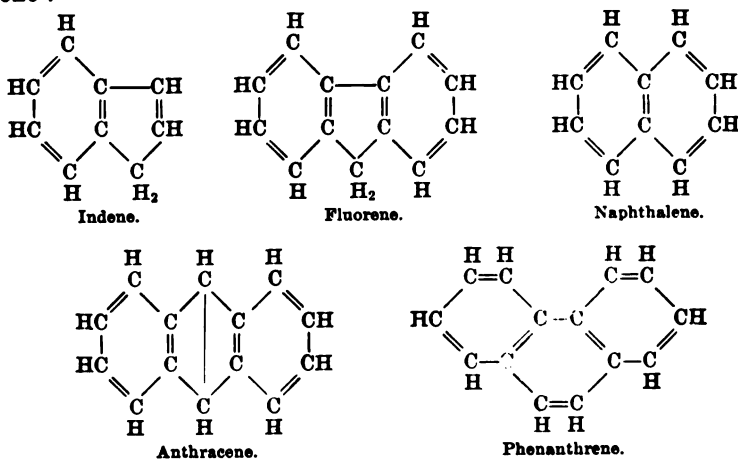
d-camphor by heating with HNO_3 . It forms colorless, odorless needles, soluble in alcohol, ether and boiling water; f. p. 187° ; $[\alpha]_D = +49.7^\circ$. By further oxidation it yields camphoronic acid, or trimethyl-tricarballic acid (p. 338).

Resins—are generally the products of oxidation of the hydrocarbons allied to pinene; are amorphous (rarely crystalline); insoluble in water; soluble in alcohol, ether, and essences. Many of them contain acids.

They may be divided into several groups, according to the nature of their constituents: (1) **Balsams**, which are usually soft or liquid, and are distinguished by containing free cinnamic or benzoic acid, e. g., *benzoin*, *liquidambar*, *Peru balsam*, *styrax*, *balsam tolu*; (2) **oleo-resins** consist of a true resin mixed with an oil, e. g., *Burgundy* and *Canada pitch*, *Mecca balsam*, and the resins of *capsicum*, *copaiba*, *cubebs*, *elemi*, *lupulin*; (3) **gum-resins**, mixtures of true resins and gums, e. g., *aloes*, *ammoniac*, *asafœdita*, *euphorbium*, *galbanum*, *guaiac*, *myrrh*, *olibanum*, *scammony*; (4) **true resins**, hard substances containing neither essences, gums nor aromatic acids, e. g., *resin*, *copal*, *dammar*, *jalap*, *lac*, *sandarac*; (5) **fossil resins**, e. g., *amber*, *asphalt*, *osocerite*.

C. COMPOUNDS WITH CONDENSED NUCLEI.

These compounds contain two or more benzene rings, or one or more benzene rings and a pentacarbo-cyclic ring, fused together in such manner that the adjacent rings have two carbon atoms in common. The parent hydrocarbons of these compounds are: indene, fluorene, naphthalene, anthracene, phenanthrene, chrysene, and picene:



The derivatives of these hydrocarbons are similar in their general properties to the benzene derivatives, with some differences in orientation. Chrysene, $C_{18}H_{12}$, and picene, $C_{22}H_{14}$, are naphthalene-phenanthrenes (p. 496). Most of these hydrocarbons form crystalline addition products with picric acid.

CONDENSED HYDROCARBONS.

These hydrocarbons accompany benzene in coal-tar. Naphthalene and anthracene are obtained from this source industrially.

Indene— C_9H_8 —(constitution, p. 493)—exists in the fraction of coal-tar, distilling between 176° and 182° . It has also been obtained synthetically. Indene derivatives can also be produced from naphthalene derivatives, one benzene ring being converted into a pentacarboyclic ring (see formulæ, p. 493). Indene is the hydrocarbon corresponding to indole, which contains NH in place of the CH_2 group (p. 538). It is an oil; b. p. 178° ; sp. gr. 1.04 at 15° . At a red heat two molecules of indene unite, with loss of $4H$, to form chrysene (p. 496). By reduction indene is converted into **hydrindene**, $C_8H_4:(CH_2)_3$; an oil; b. p. 177° .

Fluorene—**Diphenylene Methane**— $C_{13}H_{10}$ —exists in the fraction of distillation of heavy coal-tar oils, distilling between 300° and 320° . It is also formed by the action of red heat upon diphenyl methane $(C_6H_5)_2CH_2$, and from other diphenyl and phenanthrene derivatives. It crystallizes in colorless leaflets, having a violet fluorescence; f. p. 113° ; b. p. 295° ; very soluble in ether and in benzene, sparingly soluble in alcohol. Its picric acid compound forms red needles, f. p. 81° .

The constitutional formula of fluorene is given on p. 493. It may be considered as formed by fusion of two benzene rings and one pentacarboyclic ring, with absorption, consequently, of all but one of the carbon atoms of the latter. Or it may be considered as diphenylene methane, i. e., methane in which $2H$ are replaced by two

phenylene groups, externally united: $\begin{array}{c} C_6H_4 \\ | \\ C_6H_4 \end{array} \rangle CH_2$. It is, indeed, closely related to other diphenylene compounds, in which the CH_2 group is replaced by other bivalents, as by O, S, and NH, in diphenylene oxid, sulfid and imid (carbazole, p. 538). Other fluorene derivatives are also known containing both diphenylene and diphenyl (p. 501) groups, or two diphenylenes, as **diphenylene-diphenylethylenc**, $(C_6H_4)_2C:C(C_6H_5)_2$, and **bidiphenylene ethane**, $(C_6H_4)_2-CH.CH(C_6H_4)_2$.

Naphthalene— $C_{10}H_8$ —is obtained commercially from the fraction

of coal-tar distillation passing between 180° and 300° . It crystallizes in shining plates; f. p. 79° ; b. p. 218° ; volatile at all temperatures, giving off a peculiar, tarry odor (white tar, moth-balls); sparingly soluble in cold alcohol, readily soluble in hot alcohol, ether and benzene. It is used in the arts in the preparation of phthalic acid and its derivatives, of the naphthols, etc., and of a great number of naphthalene dyes, for the carburization of water-gas, and against moths. Its picric acid compound fuses at 149° .

Naphthalene is undoubtedly formed in the distillation of coal by condensation of lower hydrocarbons under the influence of heat, a formation which may be imitated by conducting a mixture of benzene vapor with acetylene, or with ethylene, through a tube heated to redness. With ethylene, cinnamene (p. 442) is formed as an intermediate product. Naphthalene derivatives are also formed by condensation of several monobenzenic derivatives with unsaturated lateral chains. Thus α -naphthol is produced from phenyl-isocrotonic acid:

$$\text{C}_6\text{H}_5\text{CH}=\text{CH}-\text{C}(\text{OH})\text{CH}_3 = \text{C}_6\text{H}_4\text{CH}=\text{CH}-\text{C}(\text{OH})\text{CH}_3 + \text{H}_2\text{O};$$
 and naphthalene itself is formed when phenylbutylene vapor is passed over heated lime:

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 = \text{C}_6\text{H}_4\text{CH}=\text{CH}-\text{CH}=\text{CH}_2 + 2\text{H}_2.$$
 Oxidizing agents convert naphthalene into naphthoquinones (p. 499), and into benzenecarboxylic acids, among others into phthalic acid, $\text{C}_6\text{H}_4(\text{COOH})_2$. Sulfuric acid forms with it sulfonic acids.

Naphthalene Homologues — formed by substitution of alkyls for hydrogen, exist in coal-tar, and are formed by the action of alkyl iodids or bromids upon naphthalene in presence of Al_2Cl_6 .

Acenaphthene — 1, 8 — (or peri-, p. 497) **Ethylene naphthylene**, C_{10}H_8 : $\begin{array}{c} \text{CH}_2(1) \\ | \\ \text{CH}_2(8) \end{array}$, is formed when α -ethyl-naphthalene is passed through a red-hot tube, and also exists in coal-tar. By oxidation, nitration, etc., it yields a series of peri-naphthalene derivatives.

Hydronaphthalenes and their substitution products are derived from naphthalene by rupture of one or more of the double bonds, in the same manner as the hydroaromatic compounds are derived from benzene (pp. 498, 486).

Anthracene — $\text{C}_{14}\text{H}_{10}$ — is obtained commercially from the "green oil" of coal-tar, distilling above 270° ; and is used in the manufacture of alizarin dyes (artificial madder). It is formed from benzene and acetylene, or methylene bromid, in presence of Al_2Cl_6 . It crystallizes in colorless plates, having a fine blue fluorescence; f. p. 213° ; b. p. 351° ; sparingly soluble in benzene and in carbon bisulfid, which are its best solvents. Oxidizing agents convert it into anthraquinone. Its picric acid compound forms red needles, f. p. 138° .

The constitution of anthracene, given on p. 493, is proven by the formation of anthraquinone, which is diphenylene diketone: $C_6H_4:(CO)_2:C_6H_4$, in which the internal bond is liberated.

Phenanthrene— $C_{14}H_{10}$ —isomeric, with anthracene, accompanies that hydrocarbon in coal-tar. It is also formed by condensation of many benzene compounds when their vapor is passed through a red-hot tube. It crystallizes in colorless plates; f. p. 99° ; b. p. 340° ; sublimes readily at lower temperatures; soluble in benzene, ether and hot alcohol, the solutions having blue fluorescence. Oxidizing agents convert it into phenanthroquinone (p. 499). Its picric acid compound forms yellow needles, f. p. 144° .

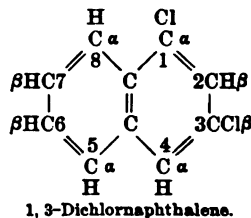
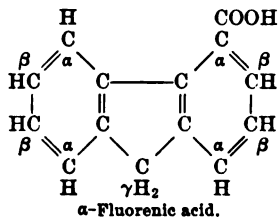
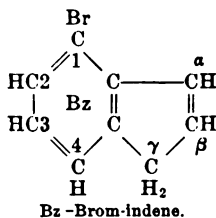
Phenanthrene is closely related to fluorene (p. 494), and to diphenyl (p. 501). It is considered as diphenyl, $HC \begin{smallmatrix} \diagup CH:CH \\ \diagdown CH:CH \end{smallmatrix} C \cdot C \begin{smallmatrix} \diagup CH:CH \\ \diagdown CH:CH \end{smallmatrix} CH$, in which the two ortho positions (o) are united by the group $-CH:CH-$, while fluorene is diphenyl in which the same positions are united by the group $-CH-$.

Chrysene— $\begin{smallmatrix} C_6H_4-CH \\ | \\ C_{10}H_6-CH \end{smallmatrix}$ —f. p. 250° ; b. p. 448° —and **Picene**— $\begin{smallmatrix} C_{10}H_6-CH \\ | \\ C_{10}H_6-CH \end{smallmatrix}$ —f. p. 364° ; resemble phenanthrene in structure, except that they contain one and two double naphthalene rings respectively in place of benzene nuclei. They exist in the coal-tar residues.

HALOID DERIVATIVES—ORIENTATION.

The complex character of the nuclei in these hydrocarbons indicates the possible existence of a greater number of isomeres than are met with in the monobenzenic series.

With **indene** different products are obtained by substitution in the benzene ring and in the three pentol positions. The former are designated by the abbreviations Bz, the latter by the Greek letters α , β , γ . Thus 1-Bz-brom-indene:

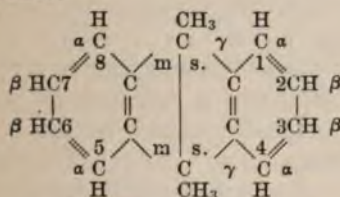
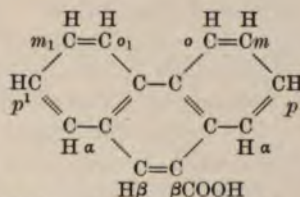


Bi-substituted derivatives are o-, m-, and p- in the benzene ring, and α , β , γ in the pentol ring. Several chlorindones are known, up to perchlorindone: $C_6Cl_4:C_3Cl_2O$.

There are three distinct positions of monosubstitution in the **fluorene** nucleus: (1) the four positions in the benzene rings nearest to the pentol ring, designated as α ; (2) the four positions furthest removed therefrom, designated as β , and (3) the single position in the pentol ring, designated as γ . A dibromid and a tribromid are known.

The **naphthalene** halids and other products of substitution have been better studied. There are two positions of monosubstitution, the four α positions nearest to the fusion of the two rings, and the four β positions, furthest removed therefrom. Both α and β fluorids, chlorids, bromids, and iodids are known. There are ten possible isomeres of each bisubstituted derivative. These are distinguished by using the numerals attached to the several positions as given above, or by the use of prefixes, as follows: 1, 2-ortho, 1, 3-meta, 1, 4-para, 1, 5-ana, 1, 6-epi, 1, 7-kata, 1, 8-peri, 2, 3-allortho, 2, 6-amphi, 2, 7-pros. The ten possible dichlorids are known. In all there are 75 possible naphthalene chlorids, of which 26 are known, and as many bromids, etc.

In **anthracene** there are three positions of monosubstitution: the four α positions nearest to the uniting groups in the benzene rings; the four β positions furthest removed therefrom; and the two γ , or "meso" (=ms.), positions in the uniting groups (see below). The γ mono- and di-chlorin and bromin compounds are formed in preference.


 ms. (or γ) Dimethyl anthracene.

 β -Phenanthrene carboxylic acid.

In **phenanthrene** there are five positions of monosubstitution: one in each of the o -, o_1 -, m -, m_1 -, p -, and p_1 - positions of the diphenyl (p. 501), the two remaining m -positions of the diphenyl, designated as α , and the two positions in the connecting group, $-C:C-$, designated as β . Chlorids are known as high as the octochlorid, and bromids as high as the heptabromid.

PHENOLS, ALCOHOLS, ALDEHYDES, KETONES, QUINONES, CARBOXYLIC ACIDS.

The **phenols**, particularly those of naphthalene, the **oxynaphthalenes**, or **naphthols**, are the most important of those compounds. The naphthols exist in coal-tar, and are also manufactured syntheti-

cally by the methods indicated below. They readily form ethers, and with ammonia they produce the corresponding naphthylamins. Both naphthols are used medicinally as antiseptics.

α -Naphthol— $C_{10}H_7(OH)_\alpha$ —is obtained by heating phenyl-isocrotonic acid (p. 495); also by boiling an aqueous solution of diazonaphthalene nitrate with nitrous acid, or by fusing α -naphthalene-sulfonic acid with KHO.

It crystallizes in colorless prisms; f. p. 95° (203° F.); b. p. 280° (536° F.); nearly insoluble in water, soluble in alcohol and in ether; is easily volatile, and has the odor of phenol. It gives a transient violet color with Fe_2Cl_6 and a hypochlorite. With nitrous acid it forms **2, 1 and 4, 1 nitroso-naphthols**. Potassium chlorate and hydrochloric acid oxidize it to dichloro-naphthoquinone. Nascent hydrogen (sodium and alcohol) reduce it to **ar-tetrahydronaphthol** (below). Its acetate fuses at 46° (114.8° F.).

β -Naphthol— $C_{10}H_7(OH)_\beta$ —is prepared industrially by fusion of sodium β -naphthalene-sulfonates with NaHO, for use in the manufacture of a number of dyes, among which are **Campobello yellow** and the **tropeolins**. It crystallizes in colorless, silky plates, which turn dark in daylight; has a faint phenol-like odor, and a sharp, burning taste; f. p. 123° (253.4° F.); b. p. 286° (514.8° F.); sparingly soluble in water, readily soluble in alcohol and in ether. It gives a greenish color with Fe_2Cl_6 . Its acetate fuses at 70° (158° F.).

Substituted Naphthols.—Both naphthols form a great number of derivatives by substitution of other groups for hydrogen atoms. Many of these are important dyes. Thus **Martius yellow** is the Na salt of **2, 4-dinitro- α -naphthol**, a poisonous pigment sometimes used to color butter and confectionery. **Naphthol yellow** is the dipotassium salt of **dinitro- α -naphthol-8-sulfonic acid**. The naphthols combine easily with the diazo- and azo-compounds (p. 481) to form a number of **azo-naphthol** derivatives, several of which are important dyes, as the **naphthol oranges** and **Bieberich scarlet**. A great variety of **naphthol-sulfonic acids** have also been prepared for use in the color industry, as in the preparation of the various **ponceau** and **Bordeaux** dyes. These sulfonic acids, being basic by their OH group and acid by the HSO_3 group, form lactone-like compounds (p. 368), which are called **sultones**.

Tetrahydronaphthols are formed by the introduction of four H atoms into one of the benzene rings, by the action of nascent hydrogen upon the naphthols. If the hydrogenation occur in the ring containing the OH, one product is obtained, designated by the prefix **ac-**, whereas if it occur in the other ring a different substance is produced, designated by the prefix **ar-**.

Anthraphenols.—Three monophenols, $C_{14}H_9(OH)$, are known:

α and β anthrols, which behave like phenols and naphthols; and μ - (or γ) oxyanthracene, or anthranol (p. 497), which is readily oxidized to anthraquinone (below). Two Bz-dioxyanthracenes, $\text{OH} \cdot \text{C}_6\text{H}_3 : (\text{CH})_2 : \text{C}_6\text{H}_3 \cdot \text{OH}$, called **chrysazol** and **rufol**, are also known.

Alcohols of this series are known: some primary: as the

Naphthyl Alcohols— $\text{C}_{10}\text{H}_7 \cdot \text{CH}_2\text{OH}$ —which are formed by the action of nitrous acid upon the corresponding amins (p. 286). The α alcohol fuses at 50° ; the β boils at 80° .

Fluorene Alcohol— $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH} \cdot \text{OH}$ —f. p. 153° , is formed by reduction of fluorene ketone (below).

Naphthyl Aldehydes— $\text{C}_{10}\text{H}_7 \cdot \text{CHO}$ —are obtained by oxidation of the alcohols. The α aldehyde boils at 291° ; the β fuses at 59° .

The **ketones** are either ring ketones, such as those of indene and fluorene, or the CO group is in a lateral chain, as in the naphthalene ketones.

γ -Indone— $\text{C}_6\text{H}_4 : \begin{array}{c} \text{CH} \\ \diagup \text{CO} \end{array} \text{CH}$ —is known in its Cl and Br derivatives; also α and β hydrindones, $\text{C}_6\text{H}_4 : \begin{array}{c} \text{CH}_2 \\ \diagup \text{CO} \end{array} \text{CH}_2$ and $\text{C}_6\text{H}_4 : \begin{array}{c} \text{CH}_2 \\ \diagup \text{CH}_2 \end{array} \text{CO}$.

Fluorene Ketone—**Diphenylene Ketone**— $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CO}$ —f. p. 84° , is formed by oxidation of fluorene with chromic acid mixture, and also from diphenic acid, $\begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{COOH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{COOH} \end{array}$.

Naphthyl-methyl Ketone— $\text{C}_{10}\text{H}_7 \cdot \text{CO} \cdot \text{CH}_3$ —is formed by the action of acetyl chlorid upon naphthalene in presence of Al_2Cl_6 .

Both aldehydes and ketones form oxims and hydrazones (pp. 409, 485).

Quinones.—Naphthalene, anthracene and phenanthrene readily yield quinones (p. 451), some of which are technically prepared by oxidizing the hydrocarbons in acetic acid solution by chromic acid; or from the dioxy- or diamido-compounds.

Naphthoquinones.—Oxidation of naphthalene produces α naphthoquinone, $\text{C}_{10}\text{H}_6 : \text{O}_{2(\alpha, 4)}$, which crystallizes in yellow needles, fusible at 125° . The α - β quinone, $\text{C}_{10}\text{H}_6 : \text{O}_{2(\alpha, \beta)}$, is formed by oxidation of β amido- α -naphthol, and crystallizes in red needles, fusible at 115° . Both naphthoquinones form oxims and hydrazones, some of which are used in the color industry.

Anthraquinone—**Diphenylene Diketone**— $\text{C}_6\text{H}_4 : (\text{CO})_2 : \text{C}_6\text{H}_4$ —is commercially manufactured by oxidation of anthracene. It forms yellow needles; f. p. 285° ; b. p. 382° . It forms an oxim with hydroxylamin, and sulfonic acids with H_2SO_4 , as well as chlorin, bromin and oxy- derivatives.

Alizarin—1, 2-Dioxyanthraquinone— $C_6H_4:(CO)_2:C_6H_2:(OH)_2$ —is prepared industrially by the action of fused NaHO upon anthraquinone-monosulfonic acid, and is also formed by fusion of several other anthraquinone derivatives with caustic alkalies. It is the coloring principle of madder (*Rubia tinctoria*), and the artificial product has now completely displaced madder in dyeing.

Purpurin—1, 2, 4-Trioxanthraquinone— $C_6H_4:(CO)_2:C_6H:(OH)_3$ —is another constituent of madder, also obtained artificially by oxidation of alizarin, or from tribromo-anthraquinone.

Both alizarin and purpurin form nitro- and amido- substitution products which are also used as dyes; alizarin, orange, blue and brown.

Several **oxymethylantraquinones** are active principles of purgative drugs. **Chrysophanic**, or **rhêic acid**, which exists in senna, rhubarb, cascara, goa-powder, is **dioxymethylantraquinone**, $C_6H_4:(CO)_2:C_6H.CH_3:(OH)_2$. Reducing agents convert it, first into **chrysarobin**, $C_{30}H_{36}O_7(?)$, which also exists in goa-powder, and finally into methylantraquinone. **Emodin**, which exist in *Rhamnus frangula* and in rhubarb, is **trioxymethylantraquinone**, $C_6H_4:(CO)_2:C_6.CH_3:(OH)_3$.

Carboxylic Acids.—A great variety of acids are derivable from indene, hydrindene, fluorene, anthracene and phenanthrene by substitution of COOH groups for hydrogen.

Naphthalene Monocarboxylic Acids—Naphthoic Acids— $C_{10}H_7-COOH$ —are formed by hydrolysis of their nitrils. The α acid fuses at 160° ; the β at 182° . Their homologues are **naphthyl-fatty acids**. They form a great variety of substitution products, nitro-, amido-, etc., among which are the **naphthol-carboxylic acids**, $C_{10}H_6-OH.COOH$, which readily decompose into water and lactones (p. 368). The **naphthalene di- and poly-carboxylic acids** are very numerous (p. 497), the best known being **naphthalic**, or **1, 8-naphthalene dicarboxylic acid**, formed by the oxidation of acenaphthene, $C_{10}H_8-(CH_2)_{1,8}$.

Naphthalene Sulfonic Acids, corresponding to the carboxylic acids, are also known. The α - and β -naphthalene monosulfonic acids, $C_{10}H_7.SO_3H$ are formed by the action of sulfuric acid on naphthalene, the latter predominating when the action occurs at 160° . These acids are converted into sulfochlorids: $C_{10}H_7.SO_2Cl$, by PCl_5 .

NITROGEN DERIVATIVES.

Naphthalene, anthracene, and phenanthrene form a number of nitro, amido, azo, and hydrazin derivatives, of which only a few of the naphthalic compounds require brief mention.

Naphthylamins—Amidonaphthalenes— $C_{10}H_7.NH_2$. Both α and β

compounds are formed by reduction of the corresponding nitro-naphthalenes, $C_{10}H_7.NO_2$; or by the action of ammonia upon the naphthols in presence of zinc chlorid: $C_{10}H_7.OH + NH_3 = C_{10}H_7.NH_2 + H_2O$, the latter a method of formation which is not realized with the amidobenzenes (p. 473). The α amin crystallizes in flat needles; f. p. 50° ($122^\circ F.$); b. p. 300° ($572^\circ F.$); insoluble in water, soluble in alcohol and ether; becomes red on exposure to air; has a persistent and disagreeable odor. On moderate oxidation it forms a blue compound, **oxynaphthylamin**, $C_{10}H_6 \begin{smallmatrix} < NH_2 \\ OH \end{smallmatrix}$; on more complete oxidation α naphthoquinone. The β amin crystallizes in plates; f. p. 112° ($233.6^\circ F.$); b. p. 294° ($561.2^\circ F.$); dissolves in hot water, forming a blue-fluorescent solution. On oxidation it forms phthalic acid. **Tetrahydro β -naphthylamin**, $C_{10}H_{11}.NH_2$, is a very active mydriatic.

Several naphthylamin-sulfonic acids are manufactured in the color industry, as well as diazo- and azonaphthalene compounds.

D. DIPHENYL AND ITS DERIVATIVES.

Diphenyl, $C_6H_5.C_6H_5$, is the type of the hydrocarbons, known as **phenylbenzenes**, formed by the substitution of phenyl, toluyl, benzyl, etc., for atoms of hydrogen in benzene (see formula of p_2 -diamidodiphenyl, p. 439). Thus we have, besides diphenyl, **toluyl-benzene**, $C_6H_5.C_6H_4.CH_3$, **diphenyl-benzene**, $C_6H_4:(C_6H_5)_2$, and **triphenyl-benzene**, $C_6H_3:(C_6H_5)_3$. These hydrocarbons are the parent substances of a great number of substitution products. The monosubstituted compounds are o-, m-, or p-, with reference to the point of union of the benzene rings. In the bi- and polysubstituted derivatives the substituents may be introduced into the same or into different rings. Bi-substitution of bivalent groups for H_2 in the o-o₂-positions produces compounds belonging to other series of our classification. Thus fluorene and phenanthrene (p. 493) are derivable from diphenyl by substitution of $-CH_2-$ and of $-CH.CH-$ respectively in the o-o₂-positions. Diphenylene oxid and sulfid and carbazole (p. 538) are similarly derivable from diphenyl by substitution of O, S, and NH.

Diphenyl—Phenylbenzene— $C_6H_5.C_6H_5$ —exists in small quantity in gas-tar. It is formed by the action of sodium upon monobromobenzene: $2C_6H_5Br + Na_2 = C_6H_5.C_6H_5 + 2NaBr$; or by passing benzene vapor through a red-hot tube; or by the interaction of diazobenzene chlorid and benzene in presence of aluminium chlorid: $C_6H_5.N:NCI + C_6H_6 = C_6H_5.C_6H_5 + HCl + N_2$. It crystallizes in large plates; f. p. 70° ($158^\circ F.$); b. p. 254° ($489.2^\circ F.$); soluble in glacial acetic acid and in amylic alcohol. Nascent hydrogen converts it into

tetrahydro-diphenyl, $C_{12}H_{14}$. With methylene chlorid, in presence of Al_2Cl_6 it forms fluorene: $C_6H_5.C_6H_5 + CH_2Cl_2 = \overline{C_6H_4.CH_2.C_6H_4} + 2HCl$. **Difluor-diphenyl**, $C_6H_4F.C_6H_4F$, is a white, crystalline powder, used as an antispasmodic under the name **antitussin**.

Amido-diphenyls, toluyls, etc., can be obtained by reduction of the corresponding nitro-compounds. One of these, **benzidin**, or **p₂-diamido-diphenyl** (formula p. 439), is a product of technical importance, which is, however, manufactured by reduction of azobenzene in acid solution. Azobenzene, $C_6H_5.N:N.C_6H_5$, first forms hydrazobenzene, $C_6H_5.NH.NH.C_6H_5$ (p. 483), which by further hydrogenation and transposition, yields benzidin, $NH_{2(4)}.C_6H_4.C_6H_4.NH_{2(4)}$. Benzidin serves for the manufacture of a number of azo dyes, which are sulfonic or carboxylic acids, or their salts. Among these benzidin dyes are Congo-yellow and Congo-red.

Oxydiphenyls are the phenols of these hydrocarbons, and are formed by fusing the benzenic phenols with KHO. The hexaoxydiphenyl derived from pyrogallol (p. 450) yields a quinone (p. 451) whose methylic ester is **cœrulignone**, $O_2:C_{12}H_6(OCH_3)_4$, the amido derivatives of which form a number of blue, violet and black dyes.

E. DIPHENYL-PARAFFINS, DIPHENYL-OLEFINS, DIPHENYL-ACETYLENES.

The hydrocarbons of this series may be considered as derived from the aliphatic hydrocarbons by substitution of two (or more) phenyl groups for hydrogen:

- $C_6H_5.CH_3$ —Phenyl-methane=Toluene=Methyl-benzene (p. 441).
- $C_6H_5.CH_2.C_6H_5$ —Diphenyl-methane=Benzyl-benzene (formula p. 439).
- $(C_6H_5)_2:CH.C_6H_5$ —Triphenyl-methane.
- $(C_6H_5)_2:Si:(C_6H_5)_2$ —Tetraphenyl-silicon (C compound unknown).
- $C_6H_5.CH_2.CH_2.C_6H_5$ —Sym. Diphenyl-ethane=Dibenzyl.
- $(C_6H_5)_2:CH.CH_3$ —Unsym. Diphenyl-ethane.
- $C_6H_5.CH:CH.C_6H_5$ —Sym. Diphenyl-ethylene=Stilbene.
- $C_6H_5.C\equiv C.C_6H_5$ —Diphenyl-acetylene=Tolane.

Diphenyl-methane—Benzyl-benzene—is produced by the action of benzyl chlorid upon benzene in presence of aluminium chlorid: $C_6H_5.CH_2.Cl + C_6H_6 = C_6H_5.CH_2.C_6H_5 + HCl$. It is a crystalline solid; f. p. 27° ($80.6^\circ F.$); b. p. 262° ($503.6^\circ F.$); soluble in alcohol, ether, and chloroform; has an odor resembling that of the orange.

Triphenyl-methane—is formed by the action of chloroform upon benzene in presence of aluminium chlorid: $3C_6H_6 + CHCl_3 = (C_6H_5)_3:CH.C_6H_5 + 3HCl$. It is a crystalline solid; f. p. 92° ($197.6^\circ F.$); b. p.

360° (680° F.); soluble in ether and in chloroform. It is converted into a trinitro-derivative by fuming HNO_3 ; and this, in turn, is converted by nascent H into leuco-pararosanilin, $\text{CH}(\text{C}_6\text{H}_4.\text{NH}_2)_3$.

Stilbene—Toluylene—Sym. Diphenyl-ethylene—is formed by distillation of benzyl sulfid; by reduction of benzoic aldehyde; or by distillation of the phenylic esters of fumaric (p. 430) or cinnamic (p. 457) acids. It forms large, glistening prisms or plates; f. p. 124° (255.2° F.); b. p. 306° (582.8° F.). It forms a number of haloid and other derivatives.

Tolane—Diphenyl-acetylene—is formed by the action of KHO upon stilbene bromid. It is a crystalline solid; f. p. 60° (140° F.).

Diphenyl-diacetylene — $\text{C}_6\text{H}_5.\text{C}\equiv\text{C}.\text{C}\equiv\text{C}.\text{C}_6\text{H}_5$ — is formed by moderate oxidation of copper phenyl-acetylid, $\text{C}_6\text{H}_5.\text{C}\equiv\text{C}.\text{Cu}.\text{C}\equiv\text{C}.\text{C}_6\text{H}_5$, as a crystalline solid; f. p. 88° (190.4° F.). Its o, o₂-dinitro-derivative is converted into indigo-blue (p. 542) by reduction.

PHENOLS, ALCOHOLS, KETONES, AND CARBOXYLIC DERIVATIVES.

Phenolic derivatives of these hydrocarbons are known, which contain hydroxyls in one or more of the phenyl groups.

Diphenyl Carbinol—Benzhydrol— $\text{C}_6\text{H}_5.\text{CHOH}.\text{C}_6\text{H}_5$ —is the simplest alcohol of this series. It is formed in colorless crystals; f. p. 68°; b. p. 298°; by reduction of benzophenone with sodium amalgam, $\text{C}_6\text{H}_5.\text{CO}.\text{C}_6\text{H}_5 + \text{H}_2 = \text{C}_6\text{H}_5.\text{CHOH}.\text{C}_6\text{H}_5$. Its **tetramethyl-diamido-** derivative, $\text{CHOH} \begin{smallmatrix} \text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2 \\ \text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2 \end{smallmatrix}$, forms colorless crystals, which dissolve in acetic acid with an intense blue color. It is formed by the action of lead peroxid and acetic acid upon **tetramethyl-diamido-diphenyl methane**, which is produced by heating dimethyl anilin with formaldehyde and a little sulfuric acid: $2\text{C}_6\text{H}_5.\text{N}(\text{CH}_3)_2 + \text{H}.\text{CHO} = \text{CH}_2 \begin{smallmatrix} \text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2 \\ \text{C}_6\text{H}_4.\text{N}(\text{CH}_3)_2 \end{smallmatrix} + \text{H}_2\text{O}$. These reactions are used as a test for formaldehyde.

Triphenyl Carbinol, $(\text{C}_6\text{H}_5)_3\text{C}.\text{OH}$, and **diphenyl-m-toluy carbinol**, $(\text{C}_6\text{H}_5)_2:\text{C}(\text{OH}).\text{C}_6\text{H}_4.\text{CH}_3$, are alcohols, whose triamido-derivatives are pararosanilin and rosanilin. They are formed by oxidation of the hydrocarbons. They form nitro- and amido-derivatives of technical importance.

The **benzophenones**, the ketones of this series, correspond to the phenones (p. 455), from which they differ in containing two phenyls in place of one; and they bear the same relation to the benzoic acids that the acetones (p. 307) do to the fatty acids. They are produced by oxidation of the hydrocarbons; by the action of P_2O_5 upon a mixture of a benzene hydrocarbon and a benzoic acid; or by the

action of phosgene or of an acidyl chlorid upon benzene in presence of aluminium chlorid.

Benzophenone—Diphenyl-ketone— $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ —forms large rhombic prisms; f. p. 48° (118.4° F.); b. p. 305° (581° F.); soluble in alcohol and ether. Sodium amalgam reduces it to **benzhydrol**, or **diphenyl carbinol**, $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{OH}$. Benzophenone is the parent substance of a great number of substitution products, some of which are used in the color industry.

Benzoin— $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ —which exists in crude oil of bitter almonds, is a keto-alcohol corresponding to **hydrobenzoin**, or **toluylene glycol**, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{C}_6\text{H}_5$, which is formed by the action of nascent H upon benzoic aldehyde (p. 453).

Benzil—Dibenzoyl— $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ —is a diketone, obtained by the action of moist silver oxid upon stilbene bromid.

Carboxylic acids derived from the diphenyl-methanes, such as **benzoyl-benzoic acids**, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, and acids derived from stilbene and from diphenyl-diacetylene are known. But few of the carboxylic acids derivable from triphenylmethanes are known, owing to their tendency to lose water and form lactones. Among these lactones are the phthaleïns and numerous other dyes, such as rosolic acid and the aurines.

The **phthalids** of this class may be considered as derived from phthalid (p. 462), $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO}_{(1)} \\ \text{CH}_2_{(2)}\end{smallmatrix}\right\rangle\text{O}$, which is the lactone of *o*-oxymethylbenzoic acid, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{COOH}_{(1)} \\ \text{CH}_2\text{OH}_{(2)}\end{smallmatrix}\right\rangle$, by substitution of phenyl for hydrogen in the CH_2 group. Thus **diphenyl phthalid**, obtained by oxidation of triphenyl methane *o*-carboxylic acid, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{COOH}_{(1)} \\ \text{CH}(\text{C}_6\text{H}_5)_{2(2)}\end{smallmatrix}\right\rangle$, has the constitution: $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO}_{(1)} \\ \text{C}_{(2)} = (\text{C}_6\text{H}_5)_2\end{smallmatrix}\right\rangle\text{O}$. The phthaleïns have been consid-

ered as oxyphenyl ketonic derivatives of phthalic acid, as indicated on p. 451, or as lactones derivable from phthalid by substitution of oxyphenyl groups. Thus phenol phthaleïn, $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO}_{(1)} \\ \text{C}_{(2)} = (\text{C}_6\text{H}_4\cdot\text{OH})_2\end{smallmatrix}\right\rangle\text{O}$

NITROGEN-CONTAINING DERIVATIVES.

Among the great number of nitro- and amido-derivatives of these hydrocarbons the most important are the amido-derivatives of triphenyl-carbinol (p. 503). From those in which two or three of the amido groups occupy the para positions with regard to the $\text{C}(\text{OH})$ group, or from their alkyl derivatives, a number of important dyes, red, green, violet, blue, and brown, are manufactured.

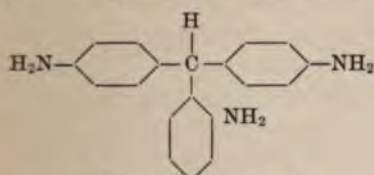
p-Amido-triphenylmethane— $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ —is formed

by the action of benzhydrol upon anilin chlorid in presence of zinc chlorid. The corresponding carbinol forms salts which have no coloring power.

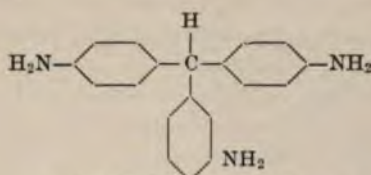
p₂-Diamido-triphenylmethane— $C_6H_5.CH:(C_6H_4.NH_{2(4)})_2$ —is produced by the interaction of anilin chlorid and benzoic aldehyde in presence of zinc chlorid, and by other methods. The base is a yellow, imperfectly crystalline solid, insoluble in water, soluble in alcohol and in benzene; which forms blue salts. The corresponding carbinol, $C_6H_5.C(OH):(C_6H_4.NH_{2(4)})_2$ forms a chlorid which is a reddish-violet dye.

p₂-Tetramethyl - diamido - triphenylmethane — $C_6H_5.CH:[C_6H_4.-N(CH_3)_{2(4)}]_2$ —is manufactured by the action of sulfuric or hydrochloric acid upon benzoic aldehyde and dimethyl-anilin. It and its carbinol are almost colorless bases, which form salts which are brilliant green dyes, **leucomalachite green** and **malachite green**, or **bitter almond-oil green**.

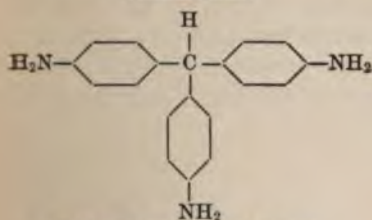
Triamido-triphenyl methanes and their alkyl derivatives (see below) are known as **leucanilins** (*λευκός*=white) from the fact that, while some of their derivatives are brilliantly colored, they are colorless, or nearly so. By oxidation they yield carbinols, formed by the substitution of OH for H in the connecting group CH, known as **rosanilins**, which are powerful triacid bases, whose salts are the dyes referred to. The most important industrially are those having at least two amido-groups in para positions. Their constitution is indicated by the following-formulae :



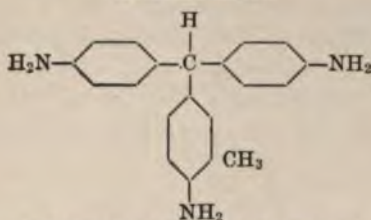
o-p₂-Triamido-triphenyl methane
(*o*-Leucanilin).



m-p₂-Triamido-triphenyl methane
(Pseudoleucanilin).

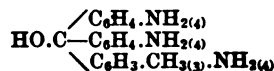
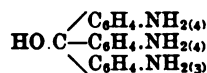
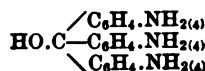
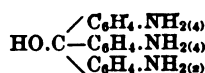


p₂-Triamido-triphenyl methane
(Paraleucanilin).



p₂-Triamido-diphenyl-*m*-toluy methane
(Leucanilin).

or, by a different form of expression for the corresponding carbinols; the **rosanilins**:

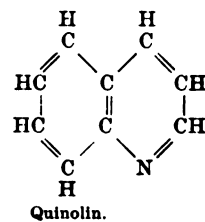
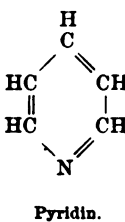
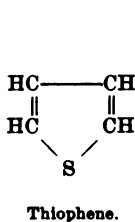
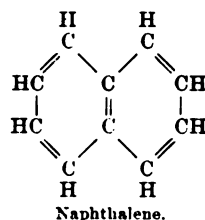
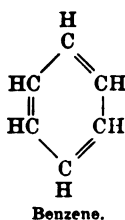
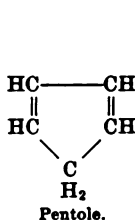


Of these the p_3 -triphenyl, and the p_3 -diphenyl-m-toluyll carbinols and their methyl, ethyl, benzyl, and phenyl derivatives are extensively used in the color industry. **Fuchsine**, **anilin red**, or **magenta** consists chiefly of the acetate or hydrochlorid of p_3 -tri-amido-diphenyl-m-toluyll carbinol, or **rosanilin**. It is manufactured by oxidation of "anilin oil" (p. 474), which is a mixture of anilin, and o- and p-toluidin, by heating with a mixture of nitro-benzene, hydrochloric acid, and iron filings. Formerly arsenic acid was used as an oxidant, when the fuchsin was obtained as a poisonous arsenite. Fuchsin forms green crystals, having a metallic luster, soluble in water and in alcohol, to which it communicates a bright-red color. This color is discharged by sulfurous acid, and regenerated by aldehydes, and such a decolorized magenta solution is used as a reagent for the detection of aldehydes (Schiff's reagent).

By the action of methyl iodid upon fuchsin a number of methylated derivatives are obtained, which are violet dyes, such as **crystal violet**, **Hofmann's violet**, **dahlia**, etc. By further methylation of the violets, green dyes are formed, as the **iodin greens**, and **aldehyde green**. By substitution of phenyl in place of methyl, a number of blue dyes, as **Lyons blue**, **soluble blue** and **alkali blue** are obtained. **Pyoktanin-blue**, **dahlia**, is penta- and hexa-methyl pararosanilin hydrochlorid, produced from dimethyl anilin. It is a violet powder, soluble in water and very diffusible, non-poisonous and used internally as an antiseptic. **Pyoktanin-yellow**, used medicinally for the same purposes as the blue, is the hydrochlorid of imido-tetramethyl-diamido-diphenyl methane, $\text{HN:C} \begin{array}{c} \diagup \text{C}_6\text{H}_4.\text{N:}(\text{CH}_3)_2 \\ - \text{C}_6\text{H}_4.\text{N:}(\text{CH}_3)_2 \end{array}$. **Tri-phenyl-pararosanilin**, $\text{HO.C:}(\text{C}_6\text{H}_4.\text{NH}.\text{C}_6\text{H}_5)_3$, is the base of a number of blue dyes, among which is **methyl-blue**, the sodium salt of its trisulfonic acid, which has been used locally in diphtheria. It is poisonous, and has caused death by its administration in mistake for methylene-blue (p. 520).

HETEROCYCLIC COMPOUNDS.

These compounds differ from the carbocyclic in that they contain elements other than carbon as constituents of the nuclei. They form series parallel to the carbocyclic, from which, indeed, they may be considered as being derived by substitution in the rings. Thus thiophene corresponds to pentole, pyridin to benzene, and quinolin to naphthalene:



The elements which can be thus introduced into a cyclic nucleus are few; oxygen, sulfur, selenium, phosphorus and nitrogen being the only ones now known to enter into such formation, and of these the nitrogen-containing compounds are far the most numerous and the most important. The facility with which the N atom takes the place of the methine group,—CH=, in the benzene ring is to be anticipated from their equivalence. Pyridin also resembles benzene in its general characters, and, on the other hand, the five membered compounds, furfurane, thiophene and pyrrole, have general characters similar to those of benzene, from which they may be considered as being derived by substitution of the bivalents O, S, and NH for one of the three acetylenes,—CH:CH—, of benzene. The number of hetero-atoms which may be contained in the nucleus is not limited to one, and five and six membered rings containing as many as four nitrogen atoms, the tetrazoles and tetrazins, are known.

A classification of the heterocyclic compounds requires many subdivisions, because of the great number and variety of these substances, due to the presence of one or more atoms of one or more

of the elements above mentioned, in three, four, five or six membered rings, contained in mono-, di-, tri-, or tetra-nucleate molecules, in which, also, differences in the ring-valence are caused by differences in internal linkage. A broad classification may, however, be here followed, somewhat similar to that for the aromatic substances (p. 439).

A. Mono-nucleate compounds: containing a single nucleus. These may be subdivided into: (a) Substances containing three-membered rings; such as ethylene oxid, $\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{array} \text{O}$, sulfid, $\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{array} \text{S}$, and imid, $\begin{array}{c} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{array} \text{NH}$.

(b) Four-membered compounds, such as trimethylene oxid, $\begin{array}{c} \text{H}_2\text{C}-\text{O} \\ | \quad | \\ \text{H}_2\text{C}-\text{CH}_2 \end{array}$, thetin, $\begin{array}{c} \text{H}_2\text{C}-\text{O} \\ | \quad | \\ \text{H}_2\text{C}-\text{S} \end{array}$, and trimethylene imid, $\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ | \quad | \\ \text{H}_2\text{C}-\text{NH} \end{array}$.

(c) Five-membered substances, such as furfurane, $\begin{array}{c} \text{HC}=\text{CH} \\ | \quad | \\ \text{HC}=\text{CH} \end{array} \text{O}$, thiophene, $\begin{array}{c} \text{HC}=\text{CH} \\ | \quad | \\ \text{HC}=\text{CH} \end{array} \text{S}$, and pyrrole, $\begin{array}{c} \text{HC}=\text{CH} \\ | \quad | \\ \text{HC}=\text{CH} \end{array} \text{NH}$.

(d) Six-membered compounds, such as pyridin, $\begin{array}{c} \text{HC}-\text{CH}=\text{CH} \\ || \quad | \\ \text{HC}-\text{CH}=\text{N} \end{array}$, piperidin, $\begin{array}{c} \text{H}_2\text{C}-\text{CH}_2-\text{CH}_2 \\ | \quad | \quad | \\ \text{H}_2\text{C}-\text{CH}_2-\text{NH} \end{array}$, and sym. tetrazin, $\begin{array}{c} \text{N}=\text{N}-\text{CH} \\ | \quad || \\ \text{HC}=\text{N}-\text{N} \end{array}$.

The five- and six-membered compounds are much more numerous and important than the three- and four-membered.

B. Condensed compounds, containing two or more rings, usually five- or six-membered, of which at least one is heterocyclic, fused together, and having two carbon atoms in common. These compounds, which correspond to the condensed benzenic compounds (p. 493), include the indole, quinolin, anthraquinolin, quinoquinolin, and diphenylene derivatives.

C. Compounds containing two (or more) nuclei, one at least heterocyclic, united directly without fusion, corresponding to the diphenyls, and including phenyl-pyridyl, dipyridyl, pyridyl-pyrrole, and pyridyl-piperidyl derivatives.

D. Compounds containing two (or more) nuclei, one at least heterocyclic, united by aliphatic groups, corresponding to the diphenyl-paraffins, and including the "ester-alkaloids" such as atropin, cocain, etc.

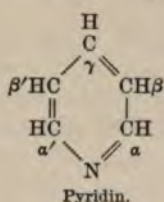
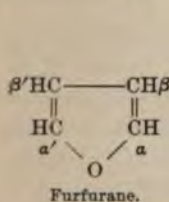
In a more detailed classification the members of the several classes are subdivided into the groups of **mono-**, **di-**, **tri-**, and **tetrahetero-atomic compounds**, according as they contain one, two, three or four atoms other than carbon, of like or different kinds, in the ring.

A.—MONONUCLEATE HETEROCYCLIC COMPOUNDS.

FIVE MEMBERED RINGS.

The parent substances of these compounds are furfurane, thiophene, and pyrrole* (see p. 508).

The heterocyclic rings differ from the carbocyclic in that the several carbon atoms are not equal in value, and therefore two different monosubstituted derivatives exist for the five membered



rings containing a single hetero-atom, such as furfurane, and three such compounds in six membered rings, such as pyridin, according to the position of substitution with reference

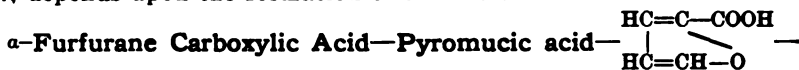
to the hetero-atom. These positions are distinguished by the first three letters of the Greek alphabet, as shown in the margin, or, sometimes by numbers. The positions α and α' , and β and β' are of equal value.

Furfurane— $\begin{array}{c} \text{HC=CH} \\ | \\ \text{HC=CH} \end{array} \text{O}$ —exists in the product of distillation of pine and fir wood, and is also formed by distillation of barium pyromucate (below), and from **dihydrofurfurane**, $\begin{array}{c} \text{HC-CH}_2 \\ || \\ \text{HC-CH}_2 \end{array} \text{O}$, a product of reduction of erythrol (p. 297). It is a liquid; b. p. 32° (89.6° F.); having a peculiar odor. Its vapor colors a pine shaving moistened with HCl green (pp. 445, 510).

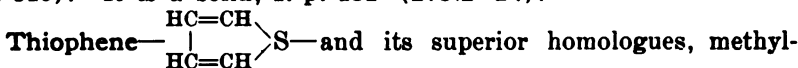
α -Furfuraldehyde—Furfurole—Furole— $\begin{array}{c} \text{HC=C-CHO} \\ | \\ \text{HC=CH-O} \end{array}$ —is produced by the dry distillation of sugar or of wood; by the distillation of these substances, or of bran, carbohydrates or glucosids with dilute H_2SO_4 ; by the action of the concentrated acid upon carbohydrates; and by distilling pentoses (p. 323), or glucuronic acid (p. 348) with HCl. It is a colorless liquid; agreeable in odor; b. p. 162° ; soluble in water and in alcohol. Being an aldehyde, it undergoes the reactions common to those substances. In concentrated solution, with urea and a trace of acid, it is colored yellow, changing to blue, to violet and to purple, and finally fading, with formation of a black precipitate (Schiff's reaction). It produces a red color with anilin, a very sensitive reaction for its presence. Paper moistened with anilin

*The usual spelling is pyrrol, furfurol, indol. The terminal e is used because these substances are neither alcohols nor phenols, for whose names the termination ol is reserved.

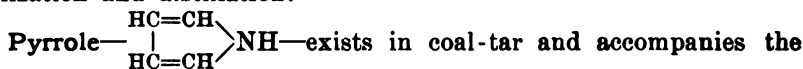
acetate solution is used. Pettenkofer's reaction for the biliary salts, etc., depends upon the formation of furfurole.



the acid corresponding to furfurole, is produced from that substance by oxidation, also by distillation of mucic and isosaccharic acids (p. 346). It is a solid; f. p. 134° (273.2° F.).



thiophenes, etc., occur in gas-tar, and accompany the various products, benzene, etc., obtained from it. It is a colorless liquid; b. p. 84° (111.2° F.); which is so nearly that of benzene, 80.5° , that the two substances cannot be separated by distillation. With sulfuric acid and isatin it gives a fine blue color, due to formation of indophenin. Sulfuric acid alone is colored brown by thiophene, which it absorbs; and thiophene may be recovered from the solution by neutralization and distillation.



pyridin bases (p. 517) in oil of Dippel. It is formed in a great variety of reactions, as by the action of baryta at 150° (303° F.) upon albumins, by the dry distillation of gelatin or of ammonium saccharate, etc. It is a colorless, oily liquid, having the odor of chloroform; b. p. 131° (267.8° F.). Being a secondary amin, it has basic properties, and its imid hydrogen is readily replaced by other atoms or groups. A pine shaving moistened with HCl is colored flame-red by pyrrole (the pine-shaving reaction; see also, Phenol, p. 445). It also yields an indigo-blue color with H_2SO_4 and isatin. Heated with dilute acids it gives off ammonia, and a red powder (pyrrole red) is deposited.

The homologous pyrroles, methyl-pyrroles, etc., have reactions similar to those of pyrrole.

Hæmopyrrole— $\text{C}_8\text{H}_{13}\text{N}$ —probably a methyl propyl pyrrole,
$$\begin{array}{c} \text{H}_3\text{C} \cdot \text{C}=\text{CH} \\ | \\ \text{H}_7\text{C}_3 \cdot \text{C}=\text{CH} \end{array} \text{NH}$$
, is a product of reduction of derivatives of the blood coloring-matter (p. 664), and of chlorophyll derivatives. It is an oil sparingly soluble in water, having a faecal odor, and gives a strong pyrrole reaction. On exposure to air it soon turns red, apparently with formation of urobilin.

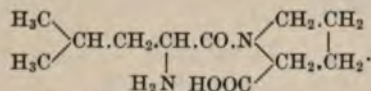
Hæmatinic Acids— $\text{C}_8\text{H}_9\text{NO}_4$ and $\text{C}_8\text{H}_8\text{O}_5$ —are derivatives of hæmopyrrole, the former an imid and the latter an anhydro acid, both monocarboxylic.

Pyrrole and its homologues form series of substitution products:

haloid, nitro-, azo-, carboxylic, etc. Among these is **tetriodopyrrole**, or **iodol**, C_4I_4NH , formed as a brown powder by acting upon pyrrole with an ethereal solution of iodine, and used in surgery as a substitute for iodoform, over which it has the advantage of being odorless.

Hydropyrrole Derivatives—Nascent hydrogen combines with pyrrole to form, first **dihydropyrrole**, or **pyrrolin**, $\begin{array}{c} CH:CH \\ | \\ CH_2.CH_2 \end{array} > NH$, an alkaline liquid, soluble in water; b. p. 91° ; and, finally, **tetrahydropyrrole**, or **pyrrolidin**, or **tetramethylene-imin**, $\begin{array}{c} CH_2.CH_2 \\ | \\ CH_2.CH_2 \end{array} > NH$, which bears the same relation to pyrrole that piperidin does to pyridin (p. 519). Pyrrolidin resembles piperidin in its reactions, and also forms an addition product with methyl iodide. It is formed by heating tetramethylene-diamin hydrochlorid (p. 386): $H_2N.(CH_2)_4.NH_2.HCl = NH_4Cl + (CH_2)_4.NH$, and constitutes the nucleus of the hygrins (p. 548) and one of those of nicotin (p. 551). It is a strongly alkaline liquid; b. p. 87° . Among the derivatives of pyrrolidin is **pyrrolidone**, or **butyrolactam**, $\begin{array}{c} CH_2.CH_2 \\ | \\ CH_2.CO \end{array} > NH$, a simple cyclic imide derived from γ -amidobutyric acid (p. 414).

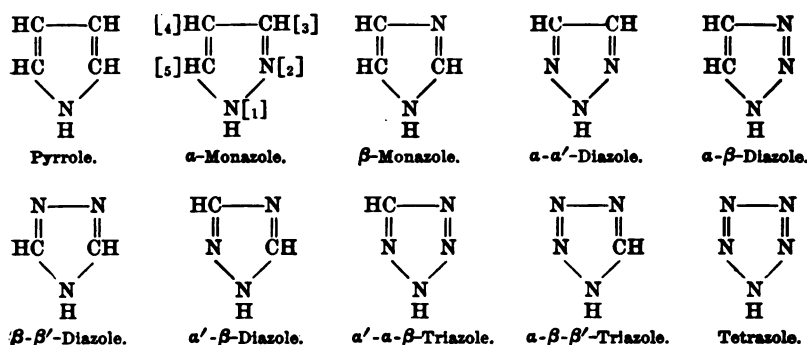
α **Pyrrolidin Carboxylic Acid—Prolin**—is a product of hydrolysis, by HCl or by tryptic digestion, of casein and gelatin, in which it probably exists as a dipeptid, constituted by substitution of the radical of α -amido-isocaproic acid for the imide hydrogen of the cyclic compound:



This compound, **leucylprolin**, has been obtained synthetically from α -pyrrolidin carboxylic acid and α -bromisocapronyl chlorid (p. 416).

AZOLES AND THEIR DERIVATIVES.

The **azoles** are derivable from furfurane, thiophene and pyrrole by substitution of one or more N atoms for methine groups in the five membered ring. They are distinguished, according to their parent substances, into **furazoles**, **thioazoles**, **pyrroazoles** and **selenazoles**, there being nine possible of each class, or they may be considered as derived from pyrrole by substitution of further hetero atoms in the ring. They are further distinguished as **monazoles**, **diazoles**, **triazoles** and **tetrazoles**, according to the number of introduced N atoms. Thus the formulæ of pyrrole and of the nine pyrroazoles are:



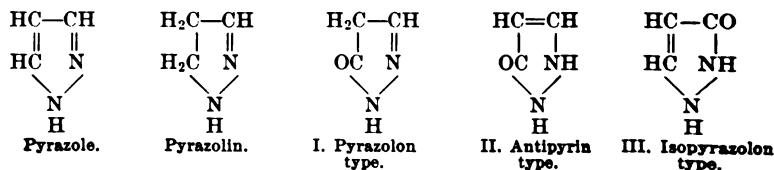
Corresponding to each of these compounds there are numerous derivatives, formed by substitution, or by modification of internal linkages and addition.

Monazoles.—The monazoles, containing N and one other hetero atom in the ring, which are known are: two **furomonazoles** (N and O), α and β , two **thiomonazoles** (N and S), α and β , two **pyrromonazoles** (N and N), α and β , and one **selenmonazole** (N and Se), β . In the α -monazoles the two hetero atoms are in adjoining positions, as in α -monazole above; and in the β -monazoles they are separated by a C atom, as in β -monazole above. The azoles of medical interest are the two pyrromonazoles and their derivatives.

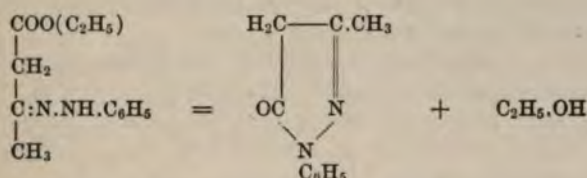
Pyrrro- α -monazole — Pyrazole — is obtained by starting from acetyl acetone and hydrazin hydrate, which by condensation yield 3, 5-dimethyl pyrazole: $\text{CH}_3\text{CO}\cdot\text{CH}_2(\text{CO}\cdot\text{CH}_3) + \text{H}_2\text{N}\cdot\text{NH}_3\text{OH} = \text{HN} \begin{array}{c} \text{N} = \text{C} \cdot \text{CH}_3 \\ \parallel \\ \text{C}(\text{CH}_3) : \text{CH} \end{array} + 3\text{H}_2\text{O}$. This is then oxidized to 3, 5-pyrazole dicarboxylic acid, which is decomposed by heat to pyrazole and carbon dioxid. It forms crystalline needles, f. p. 70° , soluble in water, alcohol and ether, has the odor of pyridin, is bitter, neutral, and a weak monacid base.

The positions of substituted groups in the derivatives of pyrazole are indicated by numbers, beginning with the imid N, as shown in the formula of α -monazole above. The most important of these derivatives are antipyrin and its congeners.

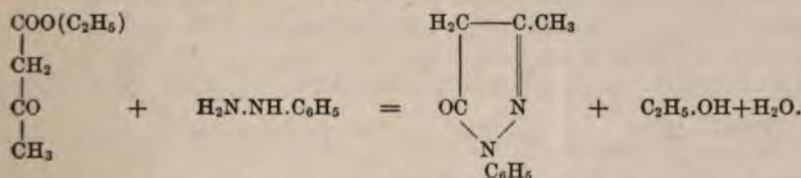
Pyrazole is reduced by sodium to **dihydropyrazole**, or **pyrazolin** (formula below), corresponding to which are three types of ketonic derivatives, or **pyrazolons**, one of which contains a single imid N, the others two each.



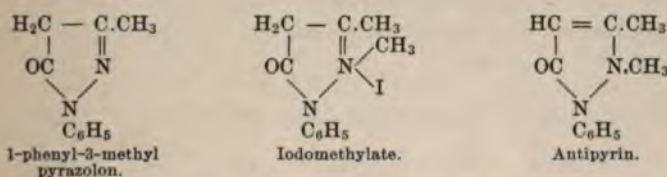
The pyrazolons are obtained from the hydrazones (p. 485) of the esters of the β ketone acids (p. 360) by elimination of alcohol, or by the action of phenylhydrazin upon these esters themselves. Thus **1-phenyl-3-methyl-pyrazolon** is formed either from phenylhydrazonacetoacetic ester:



or from aceto-acetic ester and phenylhydrazin:



Antipyrin—1-Phenyl-2,3-dimethyl Pyrazolon—(formula below)—is formed, as its hydroiodid, by heating 1, 3-phenylmethyl pyrazolon, formed by the second reaction given above, with methyl iodid and methylic alcohol to 100° (212° F.) in sealed vessels. In this reaction the I-pyrazolon type is maintained in the product of addition, but on splitting off HI to liberate the free base the antipyrin type is produced:



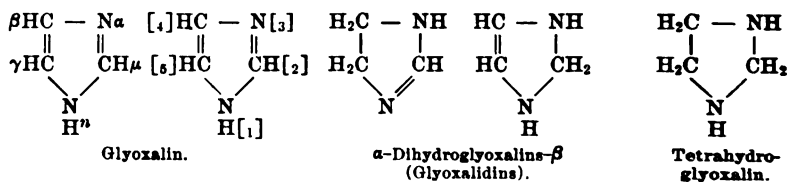
Antipyrin forms colorless, odorless scales, somewhat bitter in taste; f. p. 110.5° (230.9° F.). A mixture of equal parts of antipyrin and antifebrin (f. p. 112.5°) fuses at 45° (113° F.). Antipyrin is readily soluble in water, alcohol and chloroform, less soluble in ether. With nitrous acid or the nitrites (sp. æth. nitr.), in the presence of free acid, it forms a green, crystalline, sparingly soluble nitro-derivative, which is poisonous. Its solution is colored deep red-brown by Fe_2Cl_6 , the color being discharged by H_2SO_4 . Nitrous acid colors its solutions bright green, and on heating the mixture, after addition of a drop of fuming nitric acid, the color changes to light-red, then to blood-

red, and finally a purple oil is deposited. Addition of a drop of fuming nitric acid to cold, concentrated solution of antipyrin causes precipitation of small, green crystals. Antipyrin is strongly basic, and some of its salts are used in medicine: **Salipyrin** is antipyrin salicylate. It is formed by the action of the acid and the base upon each other at 100° (212° F.). It is a white, crystalline powder, almost insoluble in water.

Tolopyrin—1-toluy- 2, 3-dimethyl pyrazolon—is obtained in the same manner as antipyrin, using p-toluy-hydrazin in place of phenyl-hydrazin, and contains toluy, $C_6H_4.CH_3$ in place of phenyl. It forms colorless crystals; f. p. 136° (276.8° F.); and has a physiological action similar to that of antipyrin.

Pyrr- β -monazole— **β -Pyrazole**—**Imidazole**—**Glyoxalin**—(formula below)—contains the group N.C.N, which is also met with in urea and in pyrimidin and its derivatives (p. 521). Of the several known methods of its formation, the simplest is by heating glyoxal (p. 306) with ammonia and formic aldehyde: $CHO.CHO + 2NH_3 + H.CHO = HN \begin{smallmatrix} CH:N \\ | \\ CH:CH \end{smallmatrix} + 3H_2O$; or, similarly, from glyoxal and ammonia alone, in which reaction part of the glyoxal is first hydrolysed to formic acid and formic aldehyde: $CHO.CHO + H_2O = H.COOH + H.CHO$. Glyoxalin forms pearly plates, soluble in water and in ether, f. p. 89°, strongly alkaline, and having a faint fishy odor.

The orientation of the substitution products of glyoxalin and of its di- and tetrahydro derivatives is indicated by letters or numbers as shown in the formulæ below. The *n* alkyl and phenyl glyoxalins are the best known of the simpler derivatives, and are more strongly basic than the corresponding pyrazole compounds. The two possible dihydroglyoxalins and tetrahydroglyoxalin are known only in their derivatives:



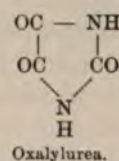
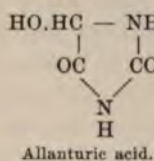
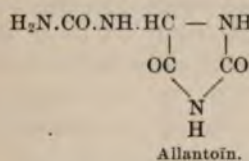
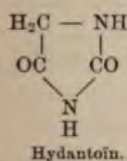
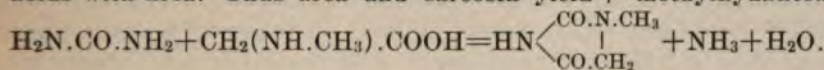
Lysidin,— **μ -Methyl- α -glyoxalidin**— $N \begin{smallmatrix} C(CH_3).NH \\ | \\ CH_2 - CH_2 \end{smallmatrix}$, is obtained by heating diacetylene diamine: $(CH_3.CO)HN.CH_2.CH_2.HN.(CO.CH_3) = \begin{smallmatrix} CH_2.NH \\ | \\ CH_2. \end{smallmatrix} N \begin{smallmatrix} C.CH_3 \\ | \\ CH_2 \end{smallmatrix} + CH_3.COOH$, or, to better advantage, by heating ethylene-diammonium chlorid with sodium acetate (p. 385).

It is a deliquescent, crystalline solid, f. p. 105° , which forms crystalline salts with acids. Its urate is the most soluble known compound of uric acid, being soluble in 6 pts. of water.

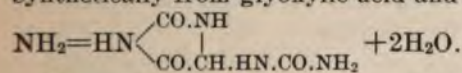
Among the **keto-hydroglyoxalins** are some which are derivatives of urea or of uric acid:

Hydantoïn, — **Glycolylurea** — **2, 5-diketotetrahydroglyoxalin** — (formula below) is the simplest of the cyclic monureids (p. 406), and is formed by the action of HI upon allantoïn, or upon alloxanic acid. It is converted into the corresponding open chain compound, hydantoic, or glycoluric acid, $\text{H}_2\text{N}.\text{CO}.\text{NH}.\text{CH}_2.\text{COOH}$, by heating with BaH_2O_2 .

Corresponding to hydantoïn are a number of substituted hydantoïns, constituted by substitution of alkyls for H in the several positions. The β -compounds are formed by heating the monoalkyl amido-acids with urea. Thus urea and sarcosin yield β -methylhydantoïn:



Allantoïn, — **Glyoxyldiureid** — (formula above) — a derivative of hydantoïn, occurs in the allantoic fluid of the cow, in the urine of sucking calves, of dogs and cats fed on meat, of children during the first few days of life, of adults after administration of tannin, and of pregnant women; also in beet juice. It is also formed during autolysis of pancreas, liver and spleen. It is obtained by oxidation of uric acid by lead peroxid: $2\text{C}_5\text{H}_4\text{N}_4\text{O}_3 + 2\text{H}_2\text{O} + \text{O}_2 = 2\text{C}_4\text{H}_6\text{N}_4\text{O}_3 + 2\text{CO}_2$, or, synthetically from glyoxylic acid and urea: $\text{CHO}.\text{COOH} + 2\text{H}_2\text{N}.\text{CO}.$



It crystallizes in prisms, sparingly soluble in cold water, readily soluble in hot water and in alcohol. On reduction by HI it yields hydantoïn and urea. Heated with alkalies it is decomposed into ammonia and carbonic, oxalic and acetic acids; glyoxylic acid being probably first formed and decomposed. Warmed with BaH_2O_2 , or with PbO_2 , it splits off urea and forms allanturic acid (formula above).

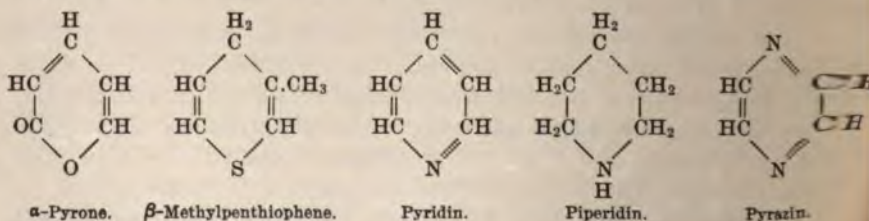
Oxalylurea, — **Parabanic Acid** — **2, 4, 5-triketotetrahydroglyoxalin** — (formula above) is formed by oxidation of uric acid or of alloxan by HNO_3 ; or synthetically by the action of POCl_3 or PCl_3 on a mixture of oxalic acid and urea: $\text{COOH}.\text{COOH} + \text{H}_2\text{N}.\text{CO}.\text{NH}_2 =$

$\text{HN} \begin{array}{c} \text{CO.NH} \\ | \\ \text{CO.CO} \end{array} + 2\text{H}_2\text{O}$. Its salts are converted into oxalates (p. 408) by water.

Histidin— $\text{C}_6\text{H}_9\text{N}_3\text{O}_2$ —one of the hexon bases (p. 417), is produced by hydrolysis of proteins. It crystallizes in rhombic plates or needles, sparingly soluble in water, insoluble in alcohol and ether, dextrorotary. It is only faintly alkaline, but expels CO_2 from Ag and Cu carbonates. By oxidation by $\text{K}_2\text{Mn}_2\text{O}_8$ in alkaline solution it yields HCN, CO_2 and NH_3 , but it is not attacked by $\text{K}_2\text{Mn}_2\text{O}_8 + \text{H}_2\text{SO}_4$. When boiled with BaH_2O_2 it does not give off NH_3 . It does not give the biuret reaction. It contains two H atoms replaceable by metals, and it forms two series of salts with acids. Nitrous acid separates one N atom as free nitrogen, and it forms one substitution product with β -naphthalene sulfonic acid; but two of its N atoms are capable of salt formation. It therefore contains one NH_2 and one NH , and the third N is tertiary. When heated it gives off CO_2 , and leaves a compound $\text{C}_5\text{H}_7\text{N}_2.\text{NH}_2$, and therefore it contains a COOH . The small proportion of H indicates a closed chain nucleus, and its reactions indicate two double linkages in the ring. It gives the Weidel reaction faintly (p. 524). When diazobenzene-sulfonic acid ($\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{SO}_3\text{H}$, or sulfanilic acid and KNO_2 : the diazo reaction, p. 743) is added to a solution of histidin in Na_2CO_3 , a coloring matter is formed which is orange in acid solution and dark cherry-red in alkaline solution. The only other product of protein hydrolysis which gives this reaction is tyrosin (p. 478). Histidin is a derivative of glyoxalin, whose constitution is probably $\text{N} \begin{array}{c} \text{CH.NH} \\ | \\ \text{CH:C.CH}_2.\text{CHNH}_2.\text{COOH} \end{array}$.

SIX MEMBERED RINGS.

Six membered heterocyclic compounds are known, containing oxygen, sulfur and nitrogen in the nucleus:



The oxygen and sulfur compounds are neither numerous nor important. Some of the former are products of condensation of aliphatic compounds, δ -lactones and δ -anhydrides (p. 368).

Pyrone (γ)—*Pyrocomane*— $O\langle\begin{smallmatrix} CH=CH \\ CH=CH \end{smallmatrix}\rangle CO$ —is an oxidized derivative of γ furane, produced from comenic acid by the action of heat and constituting the nucleus of comenic, chelidonic, and meconic acids.

Comenic acid— $C_5H_2O_2(OH).COOH$ —is produced by the action of hot H_2O , of dilute acids, or of bromin water upon meconic acid. It crystallizes in yellowish prisms, rather soluble in H_2O . It is monobasic. It is decomposed by heat into CO_2 and pyrone.

Chelidonic acid— $C_5H_2O_2(COOH)_2$ —exists in chelidonium, in combination with the alkaloids **sanguinarin** and **chelidonin**. It is a crystalline solid and a dibasic acid. Heat converts it into comenic acid, which in turn yields pyrone.

Meconic acid— $C_5HO_2(OH)(COOH)_2$ —is peculiar to opium, in which it exists in combination with a part, at least, of the alkaloids. It crystallizes in small prismatic needles; acid and astringent in taste; loses its Aq at 120° ($248^\circ F.$); quite soluble in water, soluble in alcohol, sparingly soluble in ether.

With ferric chlorid it forms a blood-red color, which is not discharged by dilute acids or by mercuric chlorid; but is discharged by stannous chlorid and by the alkaline hypochlorites.

PYRIDIN BASES AND THEIR DERIVATIVES.

The **pyridin bases**, closely related to the vegetable alkaloids (p. 545) as well as to some of the basic substances formed during putrefaction, were first obtained from **oil of Dippel**, or **bone-oil** (*Oleum animale*), an oil produced during the dry distillation of bones, horns, etc., and as a by-product in the manufacture of ammoniacal compounds from those sources. They also occur in coal-tar, naphtha, commercial ammonia, methylic spirit and fusel oil. They are formed synthetically: (1) By heating the aldehyde-ammonias (p. 409) alone, or with aldehydes or ketones; (2) From pyrrole by the action of K or Na in presence of methylene iodid, etc; (3) By oxidation of hexahydropyridins, piperidins; also by other methods.

The pyridin bases are colorless liquids of peculiar, penetrating odor. The superior homologues are metamerie with the anilins. They are strong triacid bases, and behave like tertiary monamins. Oxidizing agents do not attack pyridin, nor the nucleus of its superior homologues, but the lateral chains of the picolins, etc., are readily oxidized, with formation of **carbopyridic acids**. Reducing agents convert them into **piperidins** (p. 519). They react with several of the general reagents for the alkaloids (p. 548). The two most nearly characteristic properties of the pyridin bases are: (1) the formation of chloroplatinates such as $(C_5H_5N.HCl)_2PtCl_4$, which

on boiling with water, lose two molecules of HCl to form "modified salts" such as $(C_5H_5N)_2PtCl_4$ (Anderson's reaction), and, (2) the formation of crystalline addition products, alkyl-pyridinium iodids, such as $C_5H_5N \begin{smallmatrix} \text{CH}_3 \\ \diagup \text{I} \end{smallmatrix}$ on contact of their alcoholic solutions with alkyl iodids.

Pyridin— $HC \begin{smallmatrix} \text{CH:CH} \\ \diagdown \text{CH.CH} \end{smallmatrix} N$ —is obtained from oil of Dippel, or from piperidin. It boils at 115° (239° F.), mixes with water in all proportions, is strongly alkaline in reaction. Its hydrochlorid is crystalline, but deliquescent. Its chloroplatinate fuses at 240° (464° F.). When reduced by sodium and alcohol, it forms piperidin, or hexahydropyridin; and when reduced by hydriodic acid, normal pentane, $CH_3.CH_2.CH_2.CH_2.CH_3$.

Pyridin Homologues—Alkyl Pyridins—are substitution products containing alkyl groups for H. Owing to the inequality in value of the several C atoms of pyridin (p. 509), the number of substituted derivatives is greater than with benzene. There are three monosubstituted derivatives, six each of the bi- and tri-substituted, three tetra-, and one penta-substituted.

Methyl-pyridins—Picolins— $C_5H_4N(CH_3)$ —The three picolins, α , β and γ , exist in oil of Dippel, and have been formed synthetically. Their b. p.'s are 130° , 143° , and 144° .

Lutidins—Three ethyl pyridins, $C_5H_4N(C_2H_5)$, are known, α , b.p. 148° ; β , b.p. 166° ; and γ , b.p. 165° . Of the six possible dimethyl-pyridins, $C_5H_3N(CH_3)_2$, four are known, three of which exist in bone oil.

Collidins— $C_8H_{11}N$ —There are twenty-two possible collidins, of which twelve are known. Of these several are products of decomposition of vegetable alkaloids, or exist in oil of Dippel, or are produced during putrefaction. Conyryn, a basic substance produced by boiling coniïn (p. 549) with $ZnCl_2$, is α -propyl-pyridin. β -propyl-pyridin is produced from nicotin by passing its vapor through a red-hot tube. Aldehydin is 1, 4-methyl-ethyl-pyridin, formed by heating aldehyde-ammonia in alcoholic solution to 120° (248° F.), and from other aldehyde compounds; and exists also in the products of rectification of alcohol. An oily ptomain produced during putrefaction of gelatin in presence of pancreas is a collidin of undetermined constitution.

Parvolins— $C_9H_{13}N$.—Theory indicates the existence of 57 parvolins, of which five are known. One of these is a ptomain, produced during putrefaction of mackerel and of horse-flesh. It is an oily substance, slightly soluble in water, having, when fresh, the odor of hawthorn-blossoms, but becoming brown and resinous on exposure to air.

Coridins— $C_{10}H_{15}N$.—One of the coridins has been obtained as a product of putrefaction of fibrin and of jellyfish during several months. It is an alkaline oil, which has a poisonous action similar to that of curari. The pyridin bases in general exert a paralyzing action upon the central, and to a less degree upon the peripheral nervous system. They are the antagonists of strychnin.

Besides the alkyl-pyridins a number of **phenyl-pyridins** (p. 545) and pyridins containing unsaturated lateral chains, such as **vinyl-pyridin**, $C_5H_4N(C_2H_3)$, are known.

Pyridin Carboxylic Acids.—These acids, which bear the same relation to pyridin that the benzoic, phthalic, etc., acids bear to benzene, are formed by oxidation of the alkyl-pyridins. As most of the alkaloids contain pyridin nuclei with lateral chains, they yield pyridin-carboxylic acids upon sufficient oxidation. Thus **pyridin- β -monocarboxylic acid**, or **β -picolinic acid**, $C_5H_4N(COOH)_{(\beta)}$, is **nicotinic acid**, formed by oxidation of nicotin, of pilocarpin, as well as of β -picolin. The α acid is formed by oxidation of α -picolin. The γ acid, **isonicotinic acid**, is formed by oxidation of 3-picolin, and of many of its derivatives. **Pyridin-1, 2-dicarboxylic acid**, $C_5H_3N(COOH)_{2(1,2)}$, is **quinolinic acid**, formed by oxidation of quinolin, and **pyridin-2, 3-dicarboxylic acid** is **cinchomeronic acid**, formed by oxidation of cinchonin, cinchonidin and quinin.

Hydropyridins—**Piperidins**—are compounds produced from the pyridins by the action of nascent hydrogen. Four isomeric **dihydropyridins** are known in their derivatives: $n-\alpha$; $\beta-\gamma$; $\alpha-\beta$; and $n-\gamma$. Of the several **tetrahydropyridins** whose existence is possible the best known, in its derivatives, is the $\Delta\alpha$ compound, called **piperidein**, which polymerizes readily to **dipiperidein** with splitting out of the remaining double linkage. It is a split product of the *betel* alkaloids.

Piperidin—**Hexahydropyridin**— $H_2C \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} NH$ —which is produced by saponification of **piperin** (p. 550) by heating with alcoholic KHO, and is also formed by reduction of pyridin, or by heating **pentamethylene-diamin hydrochlorid**. It is a colorless liquid; b. p. 106° (222.8° F.); having an odor like that of pepper; readily soluble in water and in alcohol. Oxidizing agents rupture the piperidin ring, with formation of aliphatic compounds. When heated with methyl iodid is converted into **methylpiperidin hydriodid**,

$$H_2C \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} N \begin{smallmatrix} HI \\ CH_3 \end{smallmatrix}$$

Piperidin and methyl-piperidin are particularly of interest as being the nuclei of a number of vegetable alkaloids. Thus **coniin** is **α -propyl-piperidin**, and **tropin** and **ecgonin**, the basic nuclei of the atropic and cocaïn alkaloids, are derivatives of methyl-piperidin (see pp. 552, 555).

AZINS AND THEIR DERIVATIVES.

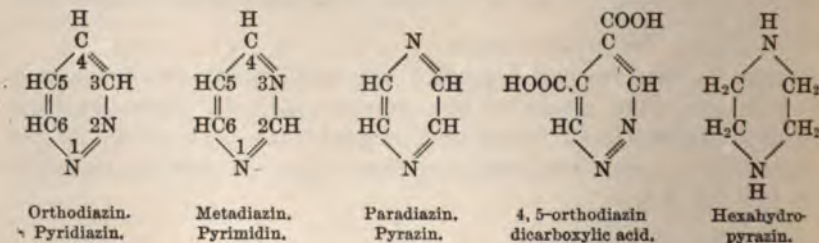
The azins are compounds bearing the same relation to pyridin that the azoles bear to pyrrole (p. 511), i. e., they are derived from pyridin by substitution of further hetero-atoms in the ring. Oxygen, sulfur and nitrogen are the only elements known to enter into such ring formation. When but one hetero-atom exists in the ring in addition to the pyridin N, the substance is a derivative of an **oxazin** if it be O, of a **thiazin** if it be S, and of a **diazin** if it be N; and there are three of each class,—ortho, meta and para. Nuclei also exist containing more than two hetero-atoms, O, S, or N, in a six membered ring, and, as these may be like or unlike, such compounds are very numerous and of great variety.

The **oxazins** and **thiazins** are only known in their derivatives. All azins enter into the constitution of condensed nuclei with benzene and with each other, particularly the paraoxazins and the parathiazins, which occur in highly complex nuclei, which may consist of as many as seven rings, in compounds used as blue, violet, red and black dyes, such as **naphthol-blue**, **Nile-blue**, **Lauth's violet**, **thionyl black**, the **safranins** and **indulins**, **methylene-blue**, etc.

Thionin, or **Lauth's violet**, is the p-amido derivative of a three-ring nucleus, the middle of which is parathiazin: $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_3 \langle \text{S} \rangle \text{C}_6\text{H}_3 \cdot \text{NH}_2$, **p-amidothiazin**. The tetramethyl derivative of this, as its chlorid, is **methylene-blue**: $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_3 \langle \text{S} \rangle \text{C}_6\text{H}_3 \cdot \text{N} : (\text{CH}_3)_2\text{Cl}$, which is formed by the oxidation of dimethyl-p-phenylenediamin, $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$, by Fe_2Cl_6 , in H_2S solution. A blue powder, sparingly soluble in water, which is used as a dye, as a bacterial stain, and medicinally as an antipyretic and antiperiodic.

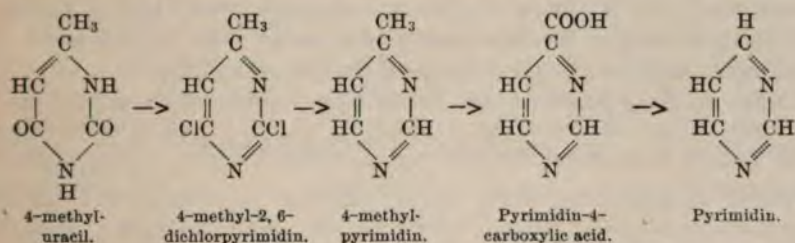
A tetrahydro-paraoxyazin ring also exists in morphin and in codein, and in **morpholin**: $\text{O} \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \text{NH}$, a product of their decomposition.

Diazins.—There exist three isomeric diazins—ortho, meta and para—which are thin colorless oils, soluble in water, alcohol and ether, insoluble in petroleum ether, neutral in reaction:



Orthodiazin—Pyridiazin—is obtained by heating the 4, 5-dicarboxylic acid (formulae p. 520): $C_4H_2N_2(COOH)_2 = C_4H_4N_2 + 2CO_2$, which is itself obtained from the tetracarboxylic acid, a product of oxidation of phenazone (below). It has a pyridin-like odor, b. p. 208° . Forms an insoluble, crystalline compound with $AuCl_3$.

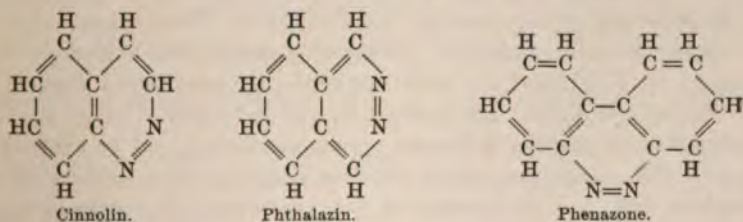
Metadiazin—Pyrimidin—is obtained by starting from 4-methyluracil. This is first converted by $POCl_3$ into 4-methyl-2, 6-dichloropyrimidin, which is then reduced by zinc dust to 4-methylpyrimidin, which is then oxidized to the carboxylic acid, and this is decomposed by heat into pyrimidin and carbon dioxide:



The free base is an oil, b. p. 124° , having a penetrating, narcotic odor, which forms a nitrate and a hydrochlorid, both of which are completely volatile below 100° . It forms crystalline compounds with $HgCl_2$, $AuCl_3$, and picric acid, but not with $CuSO_4$.

Paradiazin—Pyrazin—is obtained by condensation of amido acet-aldehyde by mercuric chlorid: $2H_2NCH_2.CHO + 2HgCl_2 = N\langle\begin{smallmatrix} CH.CH \\ CH:CH \end{smallmatrix}\rangle N + Hg_2Cl_2 + 2HCl + 2H_2O$. It has a faint heliotrope odor. B. p. 118° . From concentrated aqueous solution it deposits crystals, f. p. 53° , which are extremely volatile. It forms a crystalline compound with $CuSO_4$. Pyrazin and its homologues are produced during fermentation, and exist in fusel oils and in commercial amylic alcohol.

The three diazins form condensed products with benzene, the **benzorthodiazins**: cinnolin and phthalazin, the **benzometadiazins** and the **benzoparadiazins**, all constituted by the fusion of one benzene and one diazin ring; and also products of further condensation, containing a greater number of rings, such as phenazone:



From these, as well as from the diazins themselves, many compounds are derived by substitution, and by breaking out of double linkages and addition. The derivatives of orthodiazin and of para-diazin are not of present medical interest, except the following:

Hexahydro-pyrazin—Piperazin—Diethylene Diamin—

$$\begin{array}{c} \text{HN} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \qquad | \\ \text{H}_2\text{C} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$$

—may be obtained by reduction of para-diazin, but is manufactured from diphenyl-diethylene diamin, $\text{C}_6\text{H}_5 \cdot \text{N} \langle \text{CH}_2 \cdot \text{CH}_2 \rangle \text{N} \cdot \text{C}_6\text{H}_5$, which is obtained by the action of ethylene bromid upon anilin. It crystallizes in colorless needles; f. p. 104° ; b. p. 145° ; soluble in water, and deliquescent. It is strongly alkaline and basic, and absorbs carbon dioxid from air. It forms a soluble compound with uric acid and is used medicinally as a solvent for uric acid in lithiasis.

Keto- or Acipiperazins are ketonic derivatives of piperazin, and anhydrids of the monamido acids. **2, 5-Diacipiperazin**,
$$\begin{array}{c} \text{HN} \cdot \text{CH}_2 \cdot \text{CO} \\ | \qquad | \\ \text{OC} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$$
 is

glycocoll anhydrid (p. 412). It is obtained by evaporation of an aqueous solution of glycocoll ester: $2\text{CH}_2\text{NH}_2 \cdot \text{COO}(\text{C}_2\text{H}_5) = \text{C}_4\text{H}_6\text{N}_2\text{O}_2 + 2\text{C}_2\text{H}_5 \cdot \text{OH}$. It crystallizes in plates, sparingly soluble in water, faintly basic. This and other acipiperazins yield polypeptids on hydration (p. 415). The **leucinimid** obtained by decomposition of albumins by acids and by tryptic digestion of globin, is **3, 6-dibutyl-2, 5-diacipiperazin**, or leucin anhydrid,
$$\begin{array}{c} \text{HN} \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{CO} \\ | \qquad | \\ \text{OC} \cdot \text{CH}(\text{C}_4\text{H}_9) \cdot \text{NH} \end{array}$$
 which on hydration opens to the dipeptid leucylleucin, $\text{C}_4\text{H}_9 \cdot \text{CHNH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_4\text{H}_9 \cdot \text{COOH}$.

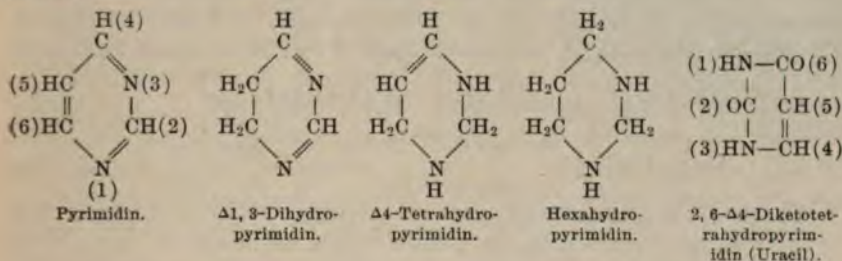
Pyrimidin Derivatives.—The **pyrimidin**, or **myazin** compounds which are of medical interest are not referable directly to pyrimidin, or metadiazin itself, but to the hydropyrimidins (formulæ p. 523), of which they are ring ketone derivatives, most of which contain the grouping $\text{N} \cdot \text{CO} \cdot \text{N}$, which also exists in urea. They include uric acid and its derivatives, the xanthin bases, and most of the cyclic ureids (p. 406). They are divided into two groups:

I. Compounds containing a single hydropyrimidin ring, more or less modified by substitution. This class includes: (a) **The uracil group**, (b) **The malonylurea group**, (c) **The guanids**.

II. **The purin group.**—Compounds containing a hydropyrimidin nucleus with a glyoxalin ring fused upon it. These compounds would be more properly classified among the condensed heterocyclic compounds (p. 537), but are more conveniently considered here.

The positions of orientation in the pyrimidin ring have been designated in several different ways, which has led to no little confusion. The notation which will be adopted here is that in which numbers are used, and in which the two nitrogen atoms occupy the

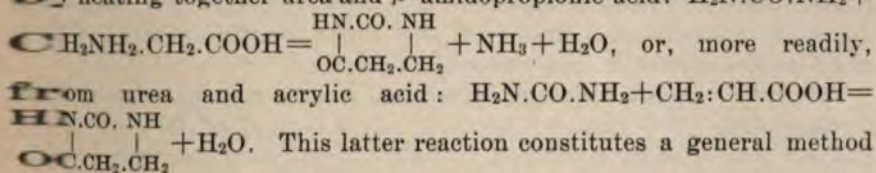
1 and 3 positions, as in the following formulæ of pyrimidin and of uracil:



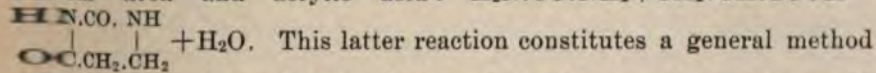
While the above hexagonal expressions are most in conformity with those of other cyclic compounds, and are on that ground preferable to the quadrilateral expression of the formula of uracil, the latter form was adopted for the uracyl, uric acid and xanthin derivatives before their relationship to pyrimidin was recognized, and have since come into such universal use that we feel reluctantly compelled to make use of them for these compounds.

I a. The Uracil Group.—The physiologically interesting members of this group are 2, 6-diketo derivatives of the unknown tetrahydropyrimidin, sometimes referred to as oxypyrimidin derivatives, a term which more properly applies to compounds containing a phenolic or secondary alcoholic OH as a lateral chain.

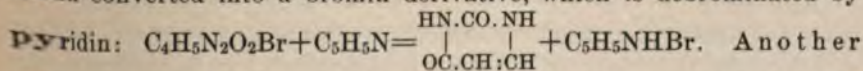
Uracil— $\text{C}_4\text{H}_4\text{N}_2\text{O}_2$ —2, 6- $\Delta 4$ -diketotetrahydropyrimidin—was first obtained as a product of decomposition of yeast-nucleic acid, and later from other nucleic acids. It is also formed from thymine in autolysis of pancreas, and is probably widely disseminated in animal organisms. It has been obtained synthetically: Hydrouracil, the corresponding hexahydropyrimidin derivative, is first obtained, either by heating together urea and β -amidopropionic acid: $\text{H}_2\text{N}.\text{CO}.\text{NH}_2 + \text{H}_2\text{N}.\text{CH}_2.\text{CH}_2.\text{COOH} =$



from urea and acrylic acid: $\text{H}_2\text{N}.\text{CO}.\text{NH}_2 + \text{CH}_2:\text{CH}.\text{COOH} =$

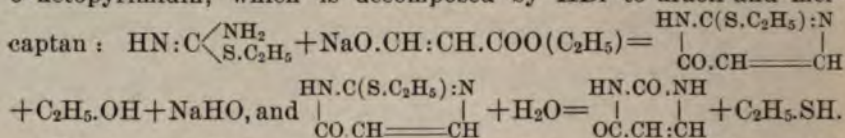


This latter reaction constitutes a general method of synthesis of uracil derivatives, starting from various unsaturated acids, known as Fischer and Roeder's method. The hydrouracil is then converted into a bromine derivative, which is debrominated by



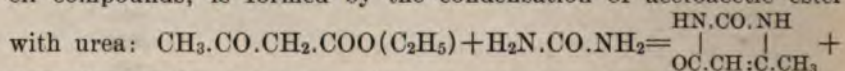
Another general method of synthesis of the uracil compounds is that of Wheeler and Johnson, based upon the fact that alkylpseudothioureas (p. 406) readily condense with ketonic acid esters (p. 360) to form

alkylmercaptoketopyrimidins, which are split by boiling with HCl or HBr to ketopyrimidins and mercaptan. Thus ethylpseudothiurea and sodium formylacetic ester (p. 362) condense to 2-ethylmercapto-6-ketopyrimidin, which is decomposed by HBr to uracil and mercaptan:



Uracil crystallizes in rosettes of needles, easily soluble in hot water, difficultly in cold water, almost insoluble in alcohol and ether, easily soluble in ammonia. It does not form compounds with HCl or HNO₃, nor a ppt. with phosphotungstic acid. With AgNO₃ alone it does not ppt., but on addition of NH₄HO a gelatinous ppt. is formed, soluble in excess. It also forms a ppt. with Hg(NO₃)₂. It gives the Weidel reaction, which consists of the production of a red or purple color when chlorin water and a trace of HNO₃ are evaporated with the substance, and the residue is exposed to ammonia. This reaction is characteristic of certain pyrimidin compounds (see Xanthin, p. 532). Two methyluracils are known.

4-Methyluracil—(formula p. 525)—the earliest known of the uracil compounds, is formed by the condensation of acetoacetic ester



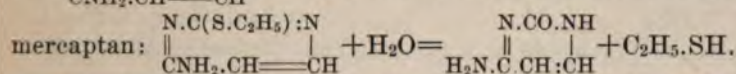
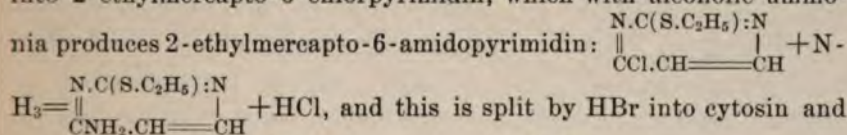
$\text{C}_2\text{H}_5\text{.OH} + \text{H}_2\text{O}$, a reaction which constitutes one of the steps in a synthesis of uric acid (p. 529). It is also formed by Fischer and Roeder's method by starting from crotonic acid, CH₃.CH:CH.COOH; and by Wheeler and Johnson's method by starting from methylpseudothiurea and acetoacetic ester. It crystallizes in needles from hot water, and is difficultly soluble in alcohol. It dissolves in NaHO or KHO, forming crystallizable salts. By further methylation it yields dimethyl- and trimethyl-uracil. It also forms chlorin, nitro, amido and phenyl derivatives, and carboxylic acids.

Thymin — 5-Methyluracil—(formula p. 525)—is a product of decomposition of thymus-nucleic acid. It is formed synthetically by Fischer and Roeder's method, starting from methylacrylic acid, CH₂:C(CH₃).COOH; and by Wheeler and Johnson's method, starting from methylpseudothiurea and sodium formylpropionic ester, $\text{NaO.CH} \begin{array}{c} \diagup \\ \text{H}_3\text{C} \end{array} \text{C.COOH}$. It crystallizes in quadratic or six-sided prisms; fuses and sublimes at 250°; is difficultly soluble in cold water, easily in hot water, less soluble in alcohol and ether. It is neither distinctly acid nor basic. Its aqueous solution ppts. with Hg(NO₃)₂; with HgCl₂ only after addition of NaHO to slight alkalinity, and with AgNO₃ only after addition of NH₄HO. It decolorizes bromin water. On

nitration and subsequent reduction it yields a compound which gives the Weidel reaction. It is pptd. by phosphotungstic acid.

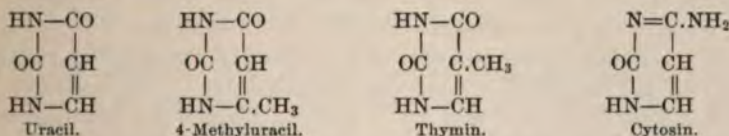
4-Phenyluracil— $C_4H_3N_2O_2.C_6H_5$ —is formed by condensation of urea and benzoylactic ester, $CH_2(CO.C_6H_5).COO(C_2H_5)$; by Fischer and Roeder's method, starting from cinnamic, or β -phenylacrylic acid, $CH(C_6H_5):CH.COOH$; and by Wheeler and Johnson's method, starting from methylpseudothiurea and sodium benzoylacetate. 5-Phenyluracil is also known.

Cytosin—6-amido-2-keto- Δ 4, 6-dihydropyrimidin—(formula below)—obtained from thymus-nucleic acids, herring and sturgeon melt, pancreas, yeast and wheat, is not properly a uracil derivative, as it does not contain two CO groups, and it is a dihydro pyrimidin, not a tetrahydropyrimidin, derivative. It is obtained synthetically by Wheeler and Johnson's method: 2-ethylmercapto-6-ketopyrimidin is obtained as described above (uracil). This is then converted by PCl_5 into 2-ethylmercapto-6-chloropyrimidin, which with alcoholic ammonia produces 2-ethylmercapto-6-amidopyrimidin:

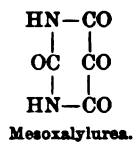
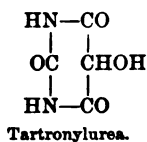
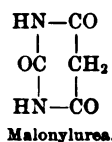


Cytosin crystallizes in pearly plates, difficultly soluble in water. It forms a hydrobromid, chloroplatinate, picrate, nitrate and two sulfates, which are all crystalline. It is pptd. by phosphotungstic acid, by $AgNO_3$, and by BaH_2O_2 in excess. It gives the Weidel reaction, although it contains but one CO. Nitrous acid converts it into uracil: $C_4H_5N_3O + HNO_2 = C_4H_4N_2O_2 + N_2 + H_2O$, as guanine is converted into xanthin, and adenin into hypoxanthin (p. 534). When oxidized by $BaMn_2O_8$ it yields biuret and oxalic acid: $C_4H_5N_3O + H_2O + 2O_2 = C_2H_5N_3O_2 + C_2O_4H_2$.

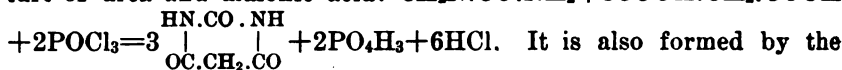
The relations of the uracils and cytosin are shown in the following formulæ:



1b. The Malonylurea Group.—The members of this group are tri- or tetraketo-hexahydropyrimidin compounds, all of which are derivable from malonylurea by substitution in the CH_2 group of malonic acid (see malonic esters, p. 361). The three principal members of the group are:



Malonylurea — Barbituric Acid — 2, 4, 6-Triketohexahydropyrimidin— $\text{C}_4\text{H}_4\text{N}_2\text{O}_3$ —is produced by the action of POCl_3 upon a mixture of urea and malonic acid: $3\text{H}_2\text{N.CO.NH}_2 + 3\text{COOH.CH}_2\text{COOH}$



It is also formed by the action of concentrated H_2SO_4 on alloxantin (p. 527). It crystallizes with 4 Aq., is efflorescent, sparingly soluble in cold water, readily soluble in hot water. It behaves as a dibasic acid. It is decomposed by boiling alkalis: $\text{C}_4\text{H}_4\text{N}_2\text{O}_3 + 3\text{H}_2\text{O} = \text{COOH.CH}_2\text{COOH} + 2\text{NH}_3 + \text{CO}_2$.

In malonylurea the hydrogen atoms of the CH_2 group exhibit the same mobility that they do in malonic ester (p. 361), and are replaceable by sodium, which is in turn replaceable by alkyls. Thus **dimethylmalonylurea**, $\text{OC} \begin{array}{c} \text{NH.CO} \\ \text{NH.CO} \end{array} \text{C}(\text{CH}_3)_2$, may be produced either by the successive action of Na and CH_3I upon malonylurea, or by the action of POCl_3 upon urea and dimethylmalonic acid. The last named acid is produced when dimethylmalonylurea is hydrolysed by KHO. Dimethylmalonylurea is isomeric with **malonyldimethylurea**, $\text{OC} \begin{array}{c} \text{N}(\text{CH}_3).\text{CO} \\ \text{N}(\text{CH}_3).\text{CO} \end{array} \text{CH}_2$, obtained by the action of POCl_3 upon malonic acid and dimethylurea. **Diethylmalonylurea**, $\text{OC} \begin{array}{c} \text{NH.CO} \\ \text{NH.CO} \end{array} \text{C}(\text{C}_2\text{H}_5)_2$, is similarly obtained, and has been used as a hypnotic under the name *veronal*.

The following derivatives of malonylurea, also produced by substitution in the CH_2 group, are of interest in connection with a synthesis of uric acid (formulæ, p. 529): **Nitromalonylurea**, formed by the action of fuming HNO_3 upon malonylurea, behaves as a tribasic acid. **Amidomalonylurea** is formed by the reduction of nitromalonylurea by HI. It yields murexid (p. 527) when boiled with ammonia; and is converted into alloxan (p. 527) by nitrous acid. It is the parent of a number of derivatives, called **uramils**, constituted by substitution of alkyls for the amid or imid hydrogen. **Pseudouric acid**, which differs from uric acid by $+\text{H}_2\text{O}$, is formed by heating amidomalonylurea with urea at 180° , or, as a salt, by heating urea with potassium cyanate. By dehydration, by heating with oxalic acid to 145° , or by boiling with concentrated HCl, it is converted into uric acid. **Methylpseudouric acids** are obtained similarly from the corresponding uramils, and serve for the synthesis of methylxanthins (p. 533).

Tartronylurea—Dialuric Acid—2, 4, 6-triketo-5-oxyhexahydropyrimidin— $C_4H_4N_2O_4$ —is produced, along with oxaluric acid (p. 408), by reduction of alloxan, it containing a secondary alcoholic group in the 5 position, where alloxan contains a ketone group (formulae p. 526). It is converted by nitrous acid into allantoin (p. 515). By exposure to air and moisture tartronylurea forms **alloxantin**, $C_8H_4N_4O_7$, in which reaction probably one molecule of tartronylurea is oxidized to alloxan, which condenses with a second molecule of tartronylurea. Alloxantin is also formed by reduction of alloxan, and by oxidation of uric acid. It forms sparingly soluble crystals, which turn red on exposure to air. **Murexid** is the ammonium salt of the unknown **purpuric acid**, $C_8H_5N_5O_6$, derived from alloxantin by substitution of NH for O, and, like that substance, containing two hydropyrimidin nuclei. It is produced by heating alloxantin with NH_3 , or by evaporating nitric acid on uric acid, and adding ammonia to the residue (murexid test, p. 530). The product of the Weidel reaction, in which chlorin water with a trace of HNO_3 is used as an oxidant (p. 524), is also probably murexid. Murexid crystallizes in short, red prisms, having a greenish reflection, and forming a red powder when ground. It is difficultly soluble in cold water, insoluble in alcohol and ether.

Alloxan—Mesoxalylurea—2, 4, 5, 6-Tetraketohexahydropyrimidin— $C_4H_2N_2O_4$ —is a product of the limited oxidation of uric acid, alloxantin, or murexid. Uric acid oxidized by dilute HNO_3 at 60° to 70° yields alloxan and urea:

$$\begin{array}{c} \text{HN.CO.C.NH} \\ | \quad \parallel \\ \text{OC.NH.C.NH} \end{array} \text{CO} + \text{H}_2\text{O} + \text{O} = \begin{array}{c} \text{HN.CO.NH} \\ | \quad | \\ \text{OC.CO.CO} \end{array}$$

+ $\text{H}_2\text{N.CO.NH}_2$. It has been found in the intestinal mucus in diarrhoea. It forms prismatic crystals, readily soluble in water, which turn red in air, are acid in reaction, and stain the skin red. Reducing agents convert it into alloxantin; and by oxidation it yields

oxalylurea: $\begin{array}{c} \text{HN.CO.NH} \\ | \quad | \\ \text{OC.CO.CO} \end{array} + \text{O} = \begin{array}{c} \text{HN.CO} \\ | \quad | \\ \text{OC.CO} \end{array} \text{NH} + \text{CO}_2$. When heated with

BaH_2O_2 the cyclic nucleus is broken, and alloxanic acid is formed:

$\begin{array}{c} \text{HN.CO.NH} \\ | \quad | \\ \text{OC.CO.CO} \end{array} + \text{H}_2\text{O} = \text{H}_2\text{N.CO.NH.CO.CO.COOH}$.

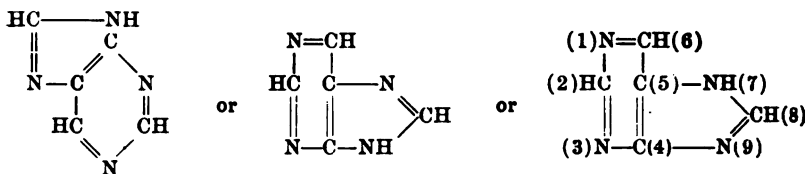
Ic. The **guanids** are derivatives of **malonylguanid**, which is **2-imido-4, 6-diketohexahydropyrimidin**, and is formed by the interaction of guanidin and malonic ester:

$(\text{C}_2\text{H}_5).\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5) + \text{HN:C} \begin{array}{l} \text{NH}_2 \\ \text{NH}_2 \end{array} = \begin{array}{c} \text{HN.C(NH).NH} \\ | \quad | \\ \text{OC.CH}_2 - \text{CO} \end{array} + 2\text{C}_2\text{H}_5.\text{OH}$

The derivatives are formed, as are those of malonic ester, and of malonylurea, by substitution in the CH_2 group.

II. The **purin group**.—The compounds of this group, which in-

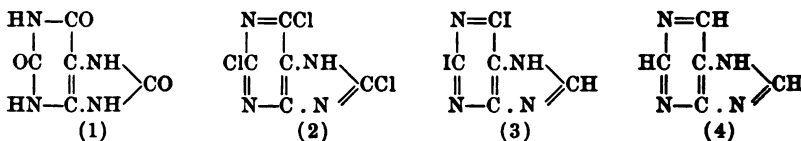
cludes uric acid, the xanthin bases, caffein, etc., are derivatives of purin, whose molecule consists of a pyrimidin ring, with a glyoxalin ring fused upon it at the 4 and 5 positions:



the last of which is the formula now generally adopted.

Some of the derivatives are referable to purin itself, others to the methylpurins, in which CH_3 is substituted for H in one or more of the positions, 2, 6, 8, and 7 or 9.

Purin— $\text{C}_5\text{H}_4\text{N}_4$ — is obtained by starting from uric acid (1). This is converted by POCl_3 , first into 8-keto-2, 6-dichlorpurin and then into 2, 6, 8-trichlorpurin (2). By the action of HI and PHI this is converted into 2, 6-diiodopurin (3), which by boiling with zinc in an atmosphere of CO_2 yields purin (4):

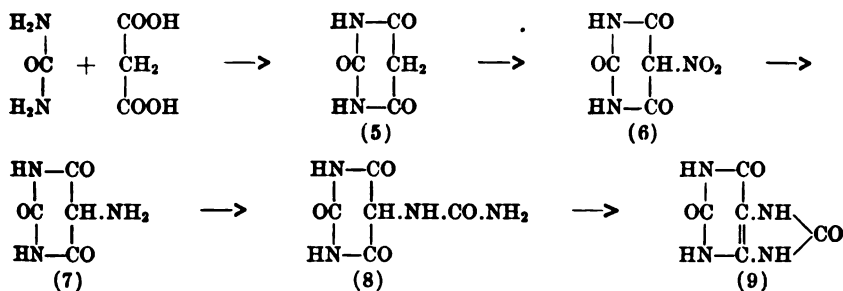


Purin crystallizes in small needles, f. p. 212° , very soluble in cold water and in warm alcohol. It is neutral in reaction, but forms salts with both acids and bases. Its solutions ppt. with AgNO_3 , phosphotungstic acid and tannin; not with KI, Nessler's reagent or $\text{K}_4\text{Fe}(\text{CN})_6$. It withstands oxidizing agents. Its reaction with Br_2 is characteristic; in its solution in concentrated HCl , Br forms a fine reddish yellow, crystalline mass, soluble on warming, and crystallizing again on cooling.

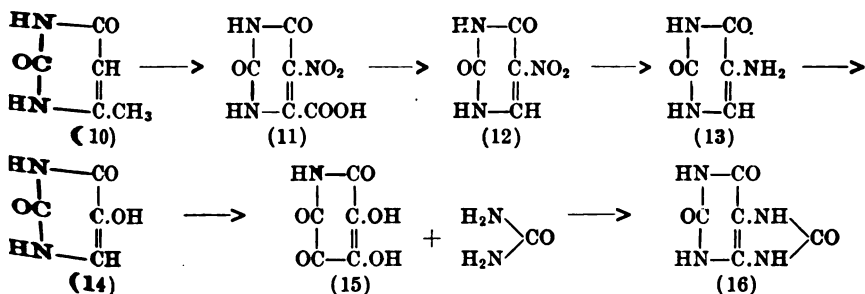
Uric Acid—*Lithic Acid*—**2,6,8-Triketopurin**—(formula 1, above), $\text{C}_5\text{H}_4\text{N}_4\text{O}_3$ —occurs in the urine of man and of the carnivora, in combination, chiefly as its disodic salt; in the urine of the herbivora, in which ordinarily it is replaced by hippuric acid, when, in early life and during starvation, they are, for the time being, practically carnivora; in some urinary calculi, in the so-called "chalky deposits," or "tophi," in the joints of the gouty; very abundantly in the excretions of serpents, tortoises, birds, molluscs and insects, and in guano; in smaller amount in the blood and tissues. It is best obtained from guano or from the solid urine of serpents, which consists almost entirely of ammonium urate.

Uric acid is obtained synthetically: (1) From monochloracet

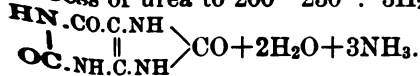
acid and urea. Monochloracetic acid is converted into malonic acid (p. 337); this is then condensed with urea to malonylurea (p. 526, and 5 below); this by HNO_3 to nitromalonylurea (6); this by reduction to amidomalonylurea (7); this by condensation with urea to pseudouric acid (8); and this by dehydration to uric acid (9):



(2) From acetoacetic ester and urea: 4-Methyluracil is first obtained from acetoacetic ester and urea (p. 524, and 10 below). By the action of fuming HNO_3 and H_2SO_4 this is converted into the 5-nitro-4-carboxylic acid (11); this by heat to 5-nitrouracil (12); this by reduction to a mixture of 5-amidouracil (13), and 5-oxyuracil, or **isobarbituric acid** (14); the former of which is converted into the latter by dilute acids. By oxidation with bromin water 5-oxyuracil yields 4, 5-dioxyuracil, or **isodialuric acid** (15), which in presence of concentrated H_2SO_4 condenses with urea to uric acid (16):



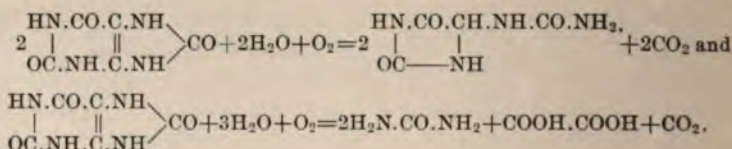
(3) From amidoacetic acid and urea, by heating glycooll with excess of urea to $200^\circ\text{--}230^\circ$: $3\text{H}_2\text{N.CO.NH}_2 + \text{CH}_2\text{NH}_2.\text{COOH} =$



When pure, uric acid crystallizes in small, colorless, rhombic, rectangular or hexagonal plates, or in rectangular prisms. As crystallized from the urine, it is more or less colored by the urinary pigments, and the angles of the crystals are rounded to produce lozenge shapes, which are arranged in bundles, crosses or daggers. It is very

sparingly soluble in water, requiring 36,480 parts of pure water for its solution at 18°. In ordinary distilled water it is more soluble, 1:15,000 cold, and 1:1,900 boiling. It is soluble in 1,900 parts of a 2 per cent solution of urea, insoluble in alcohol and ether. Cold HCl dissolves it more readily than water, and on standing deposits it in colorless rectangular plates. Its aqueous solution is acid to litmus, but tasteless and odorless. It also dissolves unchanged in concentrated H₂SO₄, and is deposited from the solution on dilution with water. It dissolves in KHO and NaHO solutions with formation of urates.

Uric acid is decomposed by heat, yielding as final products ammonia, carbon dioxide, urea and hydrocyanic and cyanuric acids. Nascent hydrogen reduces it to xanthin (p. 532). With Cl, Br, or I at ordinary temperatures it forms oxalic and parabanic acids, alloxan and ammonium cyanate. Heated with Cl it yields cyanuric acid and HCl. It dissolves in cold HNO₃, with effervescence and formation of alloxan, alloxantin and urea; with hot HNO₃ parabanic acid is produced. A yellow or red residue remains when HNO₃ is evaporated on uric acid, and this assumes a fine red-violet or purple color when moistened, in the cold, with NH₄HO, NaHO or KHO (murexid reaction). On heating with concentrated HCl to 170° uric acid is decomposed to glycocholl, ammonia and carbon dioxide: $C_5H_4N_4O_3 + 5H_2O = CH_2NH_2.COOH + 3CO_2 + 3NH_3$, and, as ammonia and carbon dioxide are the products of hydrolysis of urea, this decomposition is the reverse of the synthesis described above (p. 529). When oxidized by lead peroxid uric acid yields allantoin, carbon dioxide, urea and oxalic acid, two distinct reactions occurring at the same time:



Certain bacteria decompose uric acid according to the equation: $C_5H_4N_4O_3 + 2H_2O + O_3 = 3CO_2 + 2H_2N.CO.NH_2$. Uric acid is decomposed by sodium hypobromite, giving off 47 per cent of its nitrogen in the cold, or the whole when heated. It reduces the salts of copper on prolonged boiling in alkaline solution. The xanthin bases (p. 531) and uric acid are pptd. by a mixture of equal volumes of a 13 per cent solution of CuSO and a 50:100 solution of NaHSO₃ (Krüger-Wolff reagent), which does not ppt. urea. Uric acid is pptd. from solutions containing magnesia mixture, by ammoniacal AgNO₃, as silver-magnesium urate. It is pptd., as ammonium urate, by complete saturation of its solutions with NH₄Cl.

Uric acid behaves as a dibasic acid. The monometallic salts are formed by dissolving the acid in solutions of the metallic carbonates, or by treating solutions of the dimetallic salts with carbon dioxide. The dimetallic salts are formed by dissolving the acid in solutions of the metallic hydroxids, free from carbonate. **Mono-ammonium urate**, $C_5H_3N_4O_3(NH_4)$, exists in the solid urines of the lower animals, and in urinary sediments and calculi. It is very sparingly soluble in water. **Dipotassic urate** is alkaline in taste, absorbs CO_2 from the air, and is soluble in 44 parts of cold H_2O . **Disodic urate** forms nodular masses, soluble in 77 parts of cold water, and absorbs CO_2 from the air. It is probably in this form of combination that uric acid exists normally in the urine. **Monosodic urate** is much less soluble, requiring 1,200 parts of water for its solution. It exists, generally amorphous, in urinary sediments (amorphous urates) and calculi, and in the arthritic deposits of the gouty, sometimes beautifully crystalline. **Monocalcic urate**, soluble in 603 parts of cold water, also occurs occasionally in urinary sediments and calculi, and in "chalk stones." **Monolithic urate**, $C_5H_3N_4O_3Li$, crystallizes in needles, soluble in 60 parts of water at 50° ($122^\circ F.$), or in 368 parts at 19° ($68.2^\circ F.$). It is chiefly with a view to the formation of this, the most soluble of the monometallic urates, that the salts of lithium are given to patients suffering from the uric acid diathesis. Two salts of uric acid with organic bases are still more soluble. **Hyperazin urate** (p. 522) dissolves in 50 parts of water at 17° ($62.6^\circ F.$) and **lysidin urate** (p. 514) in 6 parts of water.

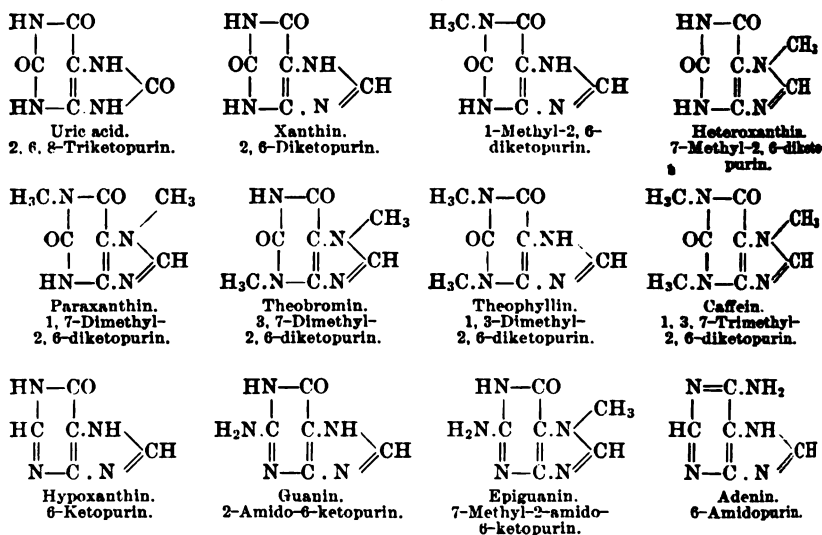
Methyluric Acids.—The four H atoms of uric acid are replaceable by methyl groups, forming three mono-, four di-, two tri-, and one tetramethyluric acids. These compounds, in which the CH_3 is attached to N, may be considered as superior homologues of uric acid, or as derivatives of the corresponding methylpurins (p. 528). They are obtained by the action of methyl iodid upon urates, or from other methylated purin compounds, notably the methylpseudouric acids, and are used in certain syntheses.

The **Xanthin, Alloxuric, Purin, or Nuclein Bases**—form a series of which uric acid is the most highly oxidized member, and which, like uric acid, are purin derivatives:

Uric acid,	$C_5H_4N_4O_3$	Heteroxanthin,	$C_5H_3(CH_3)N_4O_2$
Xanthin,	$C_5H_4N_4O_2$	Paraxanthin,	$C_5H_2(CH_3)_2N_4O_2$
Hypoxanthin,	$C_5H_4N_4O$	Theobromin,	$C_5H_2(CH_3)_2N_4O_2$
Guanin,	$C_5H_5N_5O$	Theophyllin,	$C_5H_2(CH_3)_2N_4O_2$
		Caffein,	$C_5H(CH_3)_3N_4O_2$
Adenin,	$C_5H_5N_5$	Epiguanin,	$C_5H_4(CH_3)N_5O$

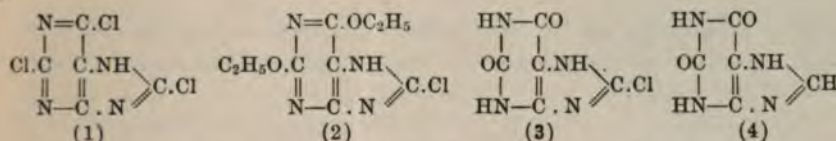
Of the substances named in the first column, xanthin, hypoxanthin and guanin are, like uric acid, ketopurins, also called oxypurins,

while adenin contains no oxygen; and guanin and adenin further differ from xanthin and hypoxanthin, in that they contain an amido group. Those in the second column are methyl derivatives of xanthin or of guanin, to which they bear the same relation that the methyluric acids do to uric acid. Besides the substances above enumerated, **carnin**, $C_7H_8N_4O_3$ and **episarkin**, $C_4H_6N_3O$ (?) probably belong in this class. Adenin, guanin, hypoxanthin and xanthin are products of decomposition of nucleic acids (p. 592), which are themselves products of decomposition of nucleoproteids (p. 591). The relations of the xanthin bases to each other and to uric acid are shown in the following formulæ:



Xanthin—*Xanthic Acid*—*Urous Acid*—**2, 6-Diketopurin**—**2, 6-Dioxyypurin**— $C_5H_4N_4O_2$ —occurs in a rare form of vesical calculus, in the pancreas, spleen, liver, thymus, kidneys, brain, and in the melt of fishes. It is a normal constituent of the urine in small amount. Xanthin, hypoxanthin, guanin and adenin are products of decomposition of the nucleius (p. 592).

Xanthin is obtained synthetically, either by the deamidation of guanin by nitrous acid (p. 535); or by Fischer's method, which, in its variations, permits of the formation of the several xanthin bases from uric acid through the chloropurins. In the formation of xanthin, uric acid is converted into 2, 6, 8-trichloropurin (1) by POCl_3 . By heating with excess of sodium ethylate this is converted into 2, 6-diethoxy-8-chloropurin (2). This is saponified by HCl to 2, 6-diketo-8-chloropurin (3), which is then reduced by HI to xanthin (4)



Xanthin and hypoxanthin are also formed in small amount by the direct reduction of uric acid by nascent formic acid. By methylation xanthin yields theobromin and caffein.

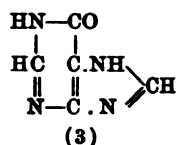
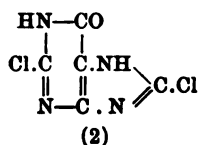
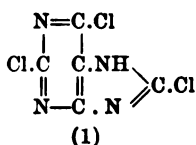
It is usually amorphous, but may form crystalline plates. It is very sparingly soluble in water, 1:14,500 at 16 degrees, 1:1,400 at 100 degrees; insoluble in alcohol or ether; readily soluble in alkalis. Its ammoniacal solution gives a gelatinous ppt. with AgNO_3 . If dissolved in HNO_3 , and the solution evaporated, it leaves a yellow residue which, with NaHO , turns reddish-yellow, then purple-red (xanthin reaction). It gives the Weidel reaction (p. 524). As this reaction is given with uracil, cytosin, uric acid, xanthin, all the methylxanthins, and alloxan, but not by hypoxanthin, guanin or adenin, it would seem to be characteristic of those pyrimidin compounds which contain the group $\text{N}.\text{CO}.\text{N}$, and notably of those containing two ketone groups, although cytosin contains but one such group.

Methylxanthins—1-Methylxanthin, 7-methylxanthin, or **heteroxanthin**, and 1, 7-dimethylxanthin, or **paraxanthin** occur in small quantities in the urine. With the xanthin reaction 1-methylxanthin gives an orange color; the others are negative. **Theobromin**, or 3, 7-dimethylxanthin, occurs in the seeds of *Theobroma cacao* in the proportion of about 2 per cent. It is a crystalline powder, bitter in taste; difficultly soluble in water, alcohol, ether and chloroform; soluble in acids, with which it forms salts; soluble in NH_4HO . By partial demethylation it yields heteroxanthin. With AgNO_3 it forms a crystalline ppt., which, heated with methyl iodid, yields caffein. **Theobromin** and caffein have both been obtained synthetically by methylation of xanthin, formed by oxidation of guanin (p. 534). **Theophyllin**, or 1, 3-dimethylxanthin, occurs in tea extract. It is formed from 1, 3-dimethyluric acid, and is manufactured for use as a diuretic, from uric acid. **Caffein**, or *thein*, or *guaranin*, or 1, 3, 7-trimethylxanthin, exists in coffee, tea, Paraguay tea, guarana and other plants, and may be produced from 1, 3, 7-trimethyluric acid. It crystallizes in long, silky needles; faintly bitter; soluble in 75 parts of water at 15 degrees; less soluble in alcohol and ether. With HNO_3 , evaporation, and addition of NH_4HO it gives a purple color.

Hypoxanthin—*Sarkin*—**6-Ketopurin**—**6-Oxypurin**— $\text{C}_5\text{H}_4\text{N}_4\text{O}$ —occurs as a constituent of the nucleins in the same situations as xanthin; also in notable amount in the blood of leukæmia, and in the

melt of salmon and carp; also in numerous seeds and pollen of plants. It is a product of the decomposition of nucleins by acids, by peptic and tryptic digestion, and by putrefaction.

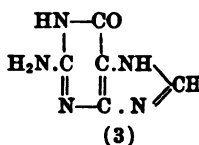
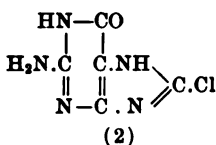
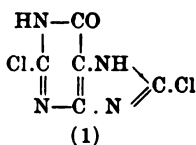
Hypoxanthin is obtained synthetically, either by deamidation of adenin by nitrous acid (adenin, p. 535); or by Fischer's method from uric acid through 2, 6, 8-trichloropurin (xanthin, p. 532), (1). This is converted into 2, 8-dichloro-6-ketopurin (2) by KHO; and this is reduced by HI and PH₄I to hypoxanthin (3):



It crystallizes in small, colorless needles; soluble in 300 parts of cold water, or in 75 parts of boiling water; soluble in acids and in alkalies. Its ammoniacal solution forms a ppt. with AgNO₃. Fuming HNO₃ oxidizes it to nitroxanthin. It does not give the Weidel reaction. When acted upon by zinc and HCl, and then treated with excess of alkali, it forms a ruby-red solution, which turns brown-red (Kossel's reaction).

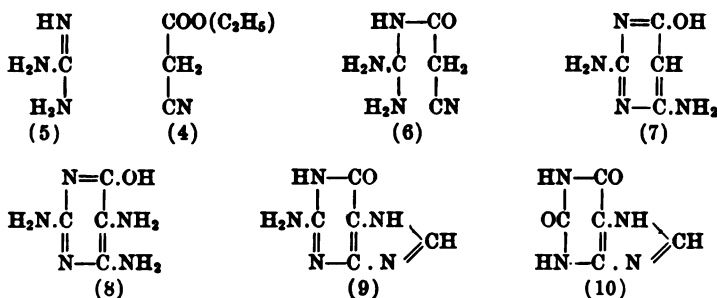
Guanin—2-Amido-6-ketopurin—occurs abundantly in guano, and as the principal constituent of the excrement of spiders; in less amount, as a constituent of guanylnucleic acid (p. 593), in the spleen, liver, pancreas, in the melt of the salmon, in the scales and swimming bladders of certain fishes, in normal urine in traces, in the blood in leukæmia; and in the young leaves and pollen of certain plants.

Guanin is produced synthetically in two ways: By Fischer's method, proceeding as in the synthesis of hypoxanthin (above) to the formation of 2, 8-dichloro-6-ketopurin (1). This is converted by heating with alcoholic ammonia at 150° into 2-amido-8-chloro-6-ketopurin (2); which is reduced by HI to guanin:

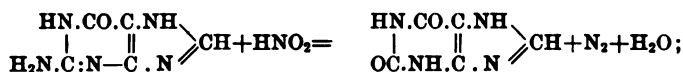


By Traube's synthesis, starting from cyanoacetic ester (4) and guanidin (5), which condense to cyanoacetic guanid (6). This, by union of the amid and cyanogen groups, forms an amidin, and the six-membered ring closes to 2, 4-diamido-6-oxypyrimidin (7). This, by addition of NaNO₂ to solution of the base, forms a rose-colored isonitroso compound, neither basic nor acid, which on reduction by

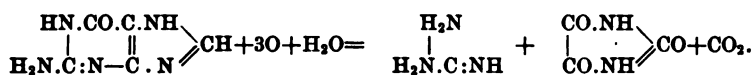
H_2S forms 2, 4, 5-triamido-6-oxypyrimidin (8), which is a strong diacid base, and which, on boiling with strong formic acid, forms guanin (9):



Guanin is deamidated by nitrous acid with formation of xanthin (10):



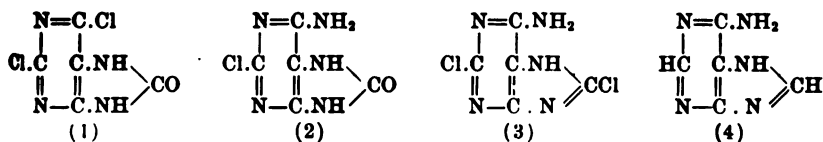
and xanthin, in turn, may be methylated to theobromin and caffeine. Guanin is oxidized by $\text{K}_2\text{Mn}_2\text{O}_8 + \text{HCl}$, with formation of guanidin and oxalylurea:



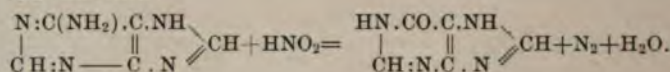
Guanin is a white or yellowish, amorphous and odorless powder: almost insoluble in water, alcohol and ether; readily soluble in acids and alkalies. It forms crystalline ppts. with silver nitrate and with picric acid. It gives the xanthin reaction with HNO_3 and NaHO ; but it does not respond to the Weidel reaction.

Adenin—6-Amidopurin— $\text{C}_5\text{H}_5\text{N}_5$ —exists, in nucleic acids, widely disseminated in nucleated cells, most abundantly in carp-melt and in the thymus gland. It occurs in the blood and urine in leukæmia, and also exists in yeast and abundantly in tea leaves.

It is formed synthetically by Fischer's method: By the action of POCl_3 upon potassium urate 2, 6-dichloro-8-ketopurin (1) is produced. This is converted into 2-chloro-6-amido-8-ketopurin (2) by NH_3 . This is converted by POCl_3 into 2, 8-dichloro-6-amidopurin (3); which is reduced by HI to adenin (4):



As guanin is deamidated to xanthin, so adenin, on deamidation, yields hypoxanthin:

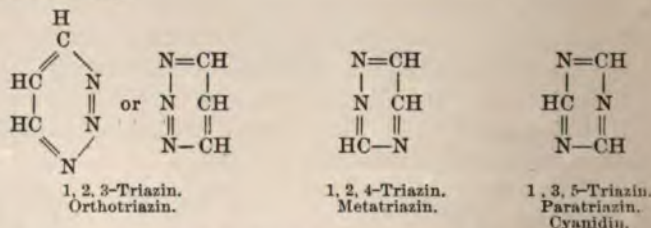


Adenin crystallizes in nacreous plates, or in long needles, with 3Aq, which they lose at 100°, although they suddenly become opaque at 53°, a property characteristic of adenin. Very soluble in hot water, it requires 1,086 parts of cold water for its solution; insoluble in cold alcohol, ether and chloroform; readily soluble in acids and alkalies, with which it forms compounds. Its solubility in ammonia is less than that of hypoxanthin, but greater than that of guanin. It forms crystalline, difficultly soluble compounds with silver nitrate and with picric acid. It is not reddened by warming with HNO₃ and moistening the residue with alkali; does not respond to the Weidel reaction, but behaves like hypoxanthin towards Kossel's reaction.

Carnin—C₇H₈N₄O₃—is obtained from Liebig's meat extract, and has also been found in the muscular tissue of fishes and frogs, and in the urine. It is isomeric with the dimethyluric acids. It forms chalky, microscopic crystals, readily soluble in hot water, sparingly soluble in cold water, insoluble in alcohol and ether. It forms compounds with acids and with alkalies, similar to those of hypoxanthin. Chlorin, bromin and nitrous acid convert it into hypoxanthin, with elimination of the elements of acetic acid. It does not respond to the Weidel reaction.

Epiguanin—C₆H₇N₅O₃.—Besides 7-methylxanthin, which is heteroxanthin, and 7-methyluric acid, similar derivatives of hypoxanthin, guanin and adenin have also been obtained synthetically. 7-Methylguanin is epiguanin, which occurs in minute quantity in the urine. **Episarkin** is possibly identical with epiguanin.

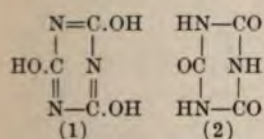
Triazines—are compounds containing three nitrogen atoms in a six-membered ring:



The parent ortho- and meta-compounds are not known, but many of their derivatives have been obtained, none of which is, however, of medical interest.

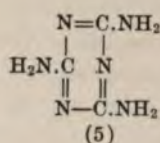
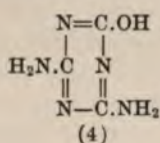
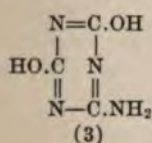
Para-, or γ -triazin, also called **cyanidin**, is the still unidentified trihydrocyanic acid, which is the parent substance of certain metalocyanids (p. 398), and of the cyanuric compounds (p. 396). Although hydrocyanic acid, pure or in concentrated solution, polymerizes readily in contact of alkalies, of KCN, etc., the product has not the constitution of cyanidin, but that of amidomalonitril: $\text{CN} \cdot \text{CH}(\text{NH}_2) \cdot \text{CN}$. The trichloro derivative is, however, known, as tricyanogen chlorid (p. 393), and the corresponding bromid and iodid are also known. The alkyl cyanidins are the polymeres of the fatty acid nitrils above acetonitril. Phenyl and phenyl-alkylcyanidins are also known, of which **triphenylcyanidin**, or **cyanophenin**, $\text{C}_3\text{N}_3(\text{C}_6\text{H}_5)_3$, was the first obtained of the compounds of this class; formed by the action of benzoyl chlorid upon potassium cyanate: $3\text{CNOK} + 3\text{C}_6\text{H}_5 \cdot \text{COCl} = \text{C}_3\text{N}_3(\text{C}_6\text{H}_5)_3 + 3\text{KCl} + 3\text{CO}_2$. It is also formed by the action of sodium upon a mixture of monoiodo-benzene and tricyanogen chlorid: $\text{C}_3\text{N}_3\text{Cl}_3 + 3\text{C}_6\text{H}_5\text{I} + 3\text{Na}_2 = \text{C}_3\text{N}_3(\text{C}_6\text{H}_5)_3 + 3\text{NaI} + 3\text{NaCl}$.

Trioxycyanidin may exist either in the *enol form* (1) or in the *ketone form* (2). The former is the probable constitution of cyanuric acid (p. 396). Corresponding to cyanuric acid are a number of alkyl,



acidyl and amido derivatives. Among the last named are **ammelid** (3), **ammelin** (4) and **melamin** (5), which are mono-, di- and triamidocyanidin respectively; each of which forms a number of derivatives by substitution of alkyls for H in NH_2 . Ammelid is one of

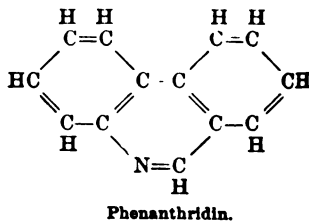
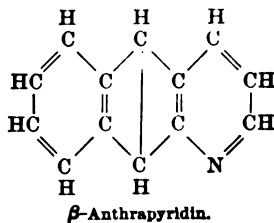
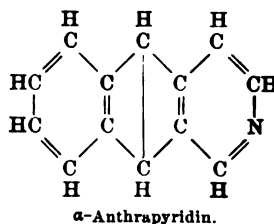
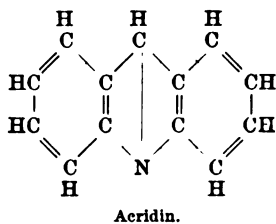
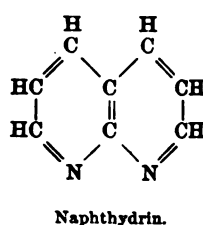
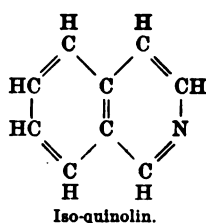
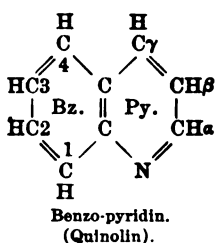
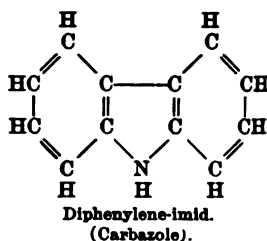
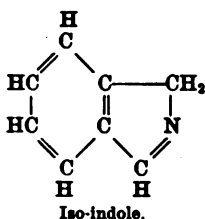
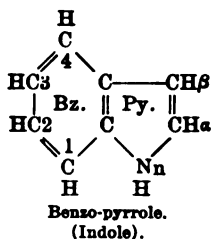
the products of the action of heat upon urea (p. 404). Melamin is obtained by the action of KHO on **melam**, $\text{C}_3\text{H}_9\text{N}_3$, which is produced by heating ammonium thiocyanate to 300° . Melamin is hydrolysed by long heating with acids or alkalies, first to ammelin, then to ammelid, and finally to cyanuric acid.



B. CONDENSED HETEROCYCLIC COMPOUNDS.

These compounds, which are more numerous than the corresponding carbocyclic compounds (p. 493), may be considered as being derived from the latter by substitution of N for methine, $=\text{CH}-$, or of O, S, or NH in a bivalent position, or, as in the case of iso-indole (p. 538), by substitution and modification of internal link-

age. The number of these substances is still further increased by the existence of four ringed-compounds, such as the anthraquinolins and indigo-blue (p. 542). The formulæ below are those of some of the nitrogen derivatives, in which indole and isoindole may be considered as derived from indene (p. 493): carbazole from fluorene; quinolin, iso-quinolin and naphthydrin from naphthalene; acridin and the anthrapyrindins from anthracene; and phenanthridin from phenanthrene:

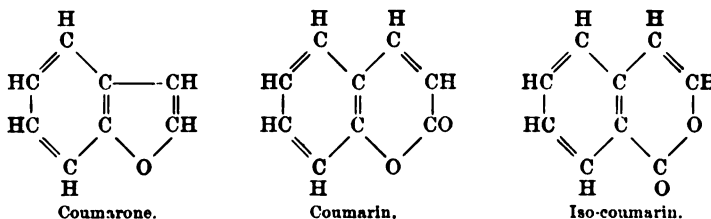


CONDENSED NUCLEI CONTAINING OXYGEN OR SULFUR MEMBERS.

Of these we will consider only a few of the oxygen compounds:

Coumarone — Benzofurfurane—(formula below)—is formed by the action of KHO upon the coumarins, and is the parent substance of two series of substitution derivatives, α and β .

Coumarin, and **isocoumarin** and their alkyl and phenolic derivatives, e.g. umbelliferone, aesculetin, daphnetin, hesperetin, exist in different vegetables (pp. 466, 467). **Coumarin** is the odorous principle of Tonka beans, and also exists in a variety of other vegetables. It is formed by the action of acetic anhydrid and sodium acetate upon salicylic aldehyde. It forms crystalline needles; f.p. 67° ; soluble in water, alcohol and ether. **Coumarin** and **isocoumarin** are benzo-derivatives of α -pyrone (p. 516):



Benzo- and dibenzo- γ -pyrones, the latter called **xanthenes**, exist in several natural yellow dyes of vegetable origin, as those from quercetin and chrysin.

CONDENSED NUCLEI CONTAINING A NITROGEN MEMBER.

BENZOPYRROLE AND ITS DERIVATIVES — INDIGO COMPOUNDS.

Indole — Benzopyrrole—(formula p. 538)—is produced: (1) by distilling oxindole over zinc-dust; (2) by heating o-nitro-cinnamic acid (p. 458) with potash and iron filings, or by similar reduction of other unsaturated o-nitro substitution products of benzene (3) by the interaction of calcium formate and phenylglycocoll (p. 478). It is one of the products of putrefaction of the proteins by anærobic bacteria, and is formed in the intestine during pancreatic digestion of those substances. It is partly eliminated with the fæces and partly reabsorbed, appearing in the urine in sulfoconjugate combination. It crystallizes in large, shining, colorless plates, having the disagreeable odor of naphthylamin. It is a weak base, and its salts are decomposed by boiling water. Its aqueous solution, acidulated with HCl, is colored rose-red by KNO_2 . By fusion with KHO

it yields anilin. It gives the "pine-shaving reaction" (p. 510). It forms a compound, crystallizing in red needles, with picric acid.

Indole Homologues—Derivatives of indole are produced by substitution either in the benzene or in the pyrrole ring. The positions are distinguished as Bz. 1, 2, 3, 4 and Py. n , α , and β (see formula p. 538). The alkyl indoles, the superior homologues of indole, are formed: (1) by heating anilin with compounds containing the group $\text{CO} \cdot \text{CH}_2\text{Cl}$. Thus chloracetone and anilin yield α -methyl-

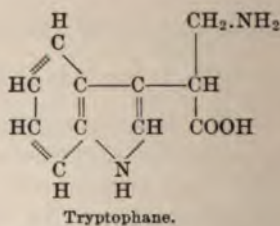
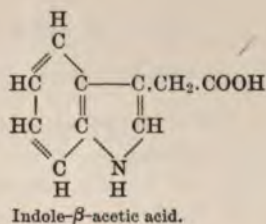
indole: $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{CH}_3 + \text{C}_6\text{H}_5 \cdot \text{NH}_2 = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CH}_3 + \text{HCl} + \text{H}_2\text{O}$;

(2) by heating the phenylhydrazones (p. 486) of the ketones, aldehydes or ketone acids with ZnCl_2 . Thus n , α -dimethylindole is obtained from acetone-phenyl-methyl-hydrazone: $\text{C}_6\text{H}_5 \cdot \text{N}(\text{CH}_3) : \text{N} : \text{C} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{N}(\text{CH}_3) \end{smallmatrix} \text{C} \cdot \text{CH}_3 + \text{NH}_3$.

The best known alkyl indoles are those in which the alkyl group is in the pyrrole ring. They dissolve in concentrated acids, and are precipitated unaltered from the solutions by dilution with water. Fused with KHO , they yield potassium salts of indole-carboxylic acids. Their hydrogen may be replaced by acidyls or by the diazo group. They give the "pine-shaving reaction," and form red, crystalline compounds with picric acid.

Indole- β -acetic acid.—The product of putrefaction, which also exists in normal urine, described as skatole carboxylic acid, is not that substance, but its isomere, indole- β -acetic acid (formula below). It produces an intense violet color with HCl and dilute Fe_2Cl_6 solution.

Tryptophane—*Proteinochromogen*—**Indole- β - β -amidopropionic Acid**—



is a product of decomposition of proteins by energetic decomposing agents such as BaH_2O_2 , H_2SO_4 , tryptic digestion and putrefaction, but not by peptic digestion. With Br or Cl it forms a red-violet pigment, called **proteinochrome**. It crystallizes in shining plates, easily soluble in hot water, difficultly in cold water or alcohol. When heated it yields indole and skatole. It gives the Adamkiewicz reaction. Its solution on a pine shaving, previously moistened with HCl , and subsequently washed and dried, gives a purple color (pyrrole reaction). By *anærobie* putrefaction it yields indole- β -propionic acid; and by

ærobie putrefaction indole- β -acetic acid, and indole. It is the parent substance of the kynuric acid found in the urine of dogs (p. 544).

β -Methyl-indole — Skatole— $\text{C}_6\text{H}_4\langle\text{C}(\text{CH}_3)\rangle_{\text{NH}}\text{CH}$ —exists in fæces, in which it exceeds the indole in amount. It is formed during putrefaction of the proteins, or by the action upon them of KHO in fusion; also by the reduction of indigo. It is best obtained synthetically by heating propidene-phenylhydrazone with zinc chlorid: $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3 = \text{C}_6\text{H}_4\langle\text{C}(\text{CH}_3)\rangle_{\text{NH}}\text{CH} + \text{NH}_3$. It crystallizes in brilliant plates; f.p. 95° (203°F.); insoluble in water, soluble in alcohol and in ether; distills with vapor of water; has a strong faecal odor. Its solution in concentrated HCl is violet. Its H_2SO_4 solution is colored deep purple when heated. Skatole, like indole, is in part reabsorbed from the intestine, and appears in the urine, combined with sulfuric and glucuronic acids.

Iso-indole—(formula, p. 538)—is formed by the action of alcoholic ammonia upon brom-acetophenone (p. 455). It crystallizes in colorless, silky plates; f. p. 195° ; insoluble in water, soluble in alcohol, ether and benzene.

Indoxyl — β -Oxyindole— $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle_{\text{NH}}\text{CH}$ —not to be confounded with oxindole (below), is a phenolic derivative of indole, obtained from indigo-blue by fusion with KHO without contact of air; or from its α -carboxylic acid, **indoxylic acid**. It is a very unstable, oily substance, soluble in water, and readily oxidized to indigo-blue (p. 542). It readily combines with sulfuric acid or the

sulfates to form **indoxyl-sulfuric acid**, $\text{C}_6\text{H}_4\langle\text{C}-\text{O}-\text{S}:\text{O}_2\rangle_{\text{NH}-\text{CH OH}}$, which is the **uroxanthin**, or **urinary indican**, existing in the urine, and formed from indole. Acids decompose it, with formation of indoxyl, which is converted into indigo-blue by Fe_2Cl_6 (see Urine).

Oxindole— $\text{C}_6\text{H}_4\langle\text{CH}_2\rangle_{\text{NH}}\text{CO}$ —the lactam of *o*-amido-phenyl acetic acid (p. 478), is obtained from dioxindole by reduction with sodium amalgam in acid solution; or by reduction of *o*-nitrophenyl-acetic acid. It crystallizes in easily soluble, colorless needles; f.p. 120° . In moist air it oxidizes to dioxindole. It reduces ammoniacal silver nitrate solution. It combines with acids and bases.

Dioxindole—Hydrindic Acid— $\text{C}_6\text{H}_4\langle\text{CH}(\text{OH})\rangle_{\text{NH}}\text{CO}$ —is the lactam *o*-amido-mandelic acid (p. 478), and is formed by the action of Na on isatin suspended in water. It forms yellow prisms, soluble in water, and combines with acids and bases.

Isatin— $\text{C}_6\text{H}_4\langle\text{CO}\rangle_{\text{NH}}\text{CO}$ —the lactam of *o*-amido-benzoyl-formic acid (p. 478), is formed by oxidation of indigo-blue by HNO_3 ; by oxidation of oxindole or of dioxindole; and by other methods. It crys-

tallizes in shining, transparent, red-brown prisms, odorless, sparingly soluble in water, readily soluble in alcohol. On further oxidation it

yields **isatoic acid**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ | \\ \text{N} \cdot \text{COOH} \end{smallmatrix}$. With hydroxylamin it forms **isatoxim**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C}=\text{NOH} \\ | \\ \text{N} \cdot \text{COH} \end{smallmatrix}$, which is also formed by the action of nitrous acid upon oxindole.

Indigo-blue—Indigotin— $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \\ | \\ \text{NH} \end{smallmatrix} \rangle \text{C} : \text{C} \begin{smallmatrix} \diagup \text{CO} \\ | \\ \text{NH} \end{smallmatrix} \rangle \text{C}_6\text{H}_4$ —constitutes the greater part of commercial indigo. It does not exist preformed in nature, but many plants, particularly *Indigofera tinctoria* and *Isatis tinctoria*, contain a yellow glucosid, indican (p. 467), which on heating with dilute acids, or probably by enzymic action on exposure to air in presence of water, is decomposed into a sugar and indigo-blue. Commercial indigo contains 20 to 90 per cent. of indigo-blue, which may be separated, nearly pure, by cautious sublimation. It is formed in several reactions, e. g., by oxidation of indoxyl by Fe_2Cl_6 and HCl ; from o-nitro-cinnamic acid by two methods; by fusing phenyl-glycocoll (p. 478) with KHO ; or by heating o-nitro-acetophenone (p. 455) with zinc dust. It forms purple-red, metallic, shining prisms or plates, odorless, tasteless, neutral, soluble in hot anilin, hot oil of turpentine, and melted paraffin, insoluble in the usual solvents. When heated it is in part converted into a dark-red vapor, and partly decomposed into anilin and other products. In the presence of aqueous alkaline solutions, reducing agents convert indigo-blue into **indigo-white**, or **di-indoxyl**, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{C(OH)} \\ | \\ \text{NH} \end{smallmatrix} \rangle \text{C} - \text{C} \begin{smallmatrix} \diagup \text{C(OH)} \\ | \\ \text{NH} \end{smallmatrix} \rangle \text{C}_6\text{H}_4$, which dissolves in the alkali. This substance absorbs oxygen from the air rapidly, with regeneration of indigo-blue. In absence of air it may be precipitated from its alkaline solution by HCl , as a white, crystalline powder, insoluble in water, but soluble in alcohol and ether, forming yellow solutions. When oxidized, as by warming with dilute HNO_3 , indigo-blue is converted into isatin, whose dilute solutions are also yellow. Hence the decoloration of indigo-blue solution is utilized as a test both for oxidizing (HNO_3) and for reducing (Mulder-Neubauer test for glucose) substances.

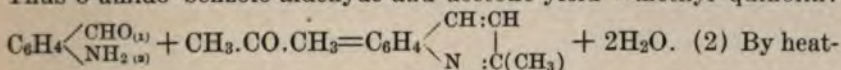
Indigo-sulfonic Acids.—Indigo-blue dissolves slowly in concentrated sulfuric acid, to a green solution, from which water precipitates a blue powder, soluble in water, but insoluble in dilute acids. This is **indigo-monosulfonic** or **phoenicin-sulfonic acid**, $\text{C}_{16}\text{H}_9\text{N}_2\text{O}_2 \cdot \text{SO}_3\text{H}$, which forms purple-red salts, soluble in water. With fuming (Nordhausen) sulfuric acid, **indigo-disulfonic**, **sulfindylic**, or **sulfindigotic acid**, $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_2(\text{SO}_3\text{H})_2$, is formed, whose K and Na salts are also soluble in water, and are met with in commerce as pastes called **indigo-carmine**.

Dibenzo-pyrrole—Diphenyl-imid—Carbazole—(formula p. 538)—exists in crude anthracene, and is formed by passing diphenylamin through a red-hot tube, and from other diphenyl derivatives. It is a crystalline solid; f. p. 238° ; soluble in alcohol and in toluene. It is a weak base, gives the pine-shaving reaction, and the blue color with isatin and H_2SO_4 , and forms a picrate fusible at 182° .

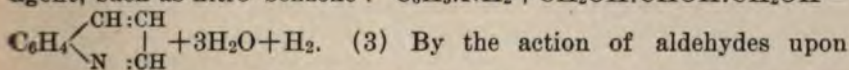
QUINOLIN AND ISO-QUINOLIN AND THEIR DERIVATIVES.

The quinolin, or benzo-pyridin bases accompany the pyridin bases (p. 517) in bone-oil, and like those substances, are closely related to the vegetable alkaloids. Quinolin, the parent substance of the group, was first obtained by distilling quinin and cinchonin with lime.

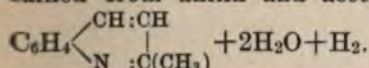
Chemically the quinolins are also related to the naphthalenes (p. 494), and are formed by similar synthetic methods. Thus quinolin is formed from allyl-anilin: $\text{C}_6\text{H}_5.\text{NH}.\text{CH}_2.\text{CH}:\text{CH}_2 = \text{C}_6\text{H}_4 \begin{smallmatrix} \text{N}:\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix} + 2\text{H}_2$, in the same manner as naphthalene is formed from phenyl-butylene (p. 495). Quinolin and its derivatives may also be produced synthetically: (1) From o-amido-benzenic compounds containing an oxygen atom in the second lateral chain. Thus o-amido-benzoic aldehyde and acetone yield α -methyl-quinolin:



ing the anilins with glycerol and H_2SO_4 , in presence of an oxidizing agent, such as nitro-benzene: $\text{C}_6\text{H}_5.\text{NH}_2 + \text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH} =$



anilins in presence of H_2SO_4 or HCl . Thus α -methyl-quinolin is obtained from anilin and acetic aldehyde: $\text{C}_6\text{H}_5.\text{NH}_2 + 2\text{CHO}.\text{CH}_3 =$



The quinolin bases are liquids of penetrating odor, sparingly soluble in water, readily soluble in alcohol and in ether. They are strong triacid bases, and form salts and ammonium-like compounds.

Quinolin— $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{N}:\text{CH} \end{smallmatrix}$ —is a mobile liquid; b. p. 238° (460.4°

F.); becoming rapidly brown on exposure to air; has an intensely acid and bitter taste, and an odor somewhat like that of bitter almonds; sparingly soluble in water, readily soluble in alcohol and ether. Its dichromate crystallizes in yellow needles; f. p. 165° ; very sparingly soluble in water.

Quinolin Homologues.—Quinolin is the nucleus of a vast number of products of substitution, among which are many isomeres, due to differences in orientation, according as the substitution occurs in the o-, m-, or p- position in the benzene ring, or in the α , β , or γ position in the pyridin ring (see formula, p. 538). Thus there are seven methyl-quinolins, or lepidins, etc.

Quinolin is of medical interest chiefly in connection with the vegetable alkaloids of which it is the nucleus (p. 556). Certain synthetic basic substances containing the quinolin nucleus have also been used in medicine, in saline combination, as antiperiodics and antipyretics. Among these are **thallin**, **ethyl-thallin** and **kairin**.

α -Oxyquinolin—Carbostyryl— C_6H_4 $\begin{array}{c} \text{CH:CH} \\ | \\ \text{N} \text{ :C.OH} \end{array}$ — is the lactam of o-amido-cinnamic acid, formed by reduction of o-nitro-cinnamic ester.

Kynuric Acid—Kynurenic Acid— $\text{C}_{10}\text{H}_7\text{NO}_3$ —has been found in the urine of dogs only. It is increased in amount of dog's urine, and appears in rabbit's urine after administration of tryptophane (p. 540). It has been obtained synthetically by a method which shows it to be

γ -oxy- β -quinolin carboxylic acid: C_6H_4 $\begin{array}{c} \text{C(OH):C.COOH} \\ | \\ \text{N} = \text{CH} \end{array}$. When heated it splits off CO_2 , and forms **kynurin**, or γ -oxyquinolin. It forms crystals, insoluble in water, soluble in hot alcohol. Its Ba salt crystallizes in triangular plates. Heated with $\text{HCl} + \text{KClO}_3$ to dryness, it leaves a reddish residue which turns green with ammonia (Jaffé's reaction).

Iso-quinolin— C_6H_4 $\begin{array}{c} \text{CH:CH} \\ | \\ \text{CH:N} \end{array}$ — differs from quinolin in that the attachment of the benzene and the pyridin rings is by the β and γ positions of the latter in iso-quinolin, and by the α and β positions in quinolin (see formulæ, p. 538). It accompanies quinolin in coal-tar, and is the nucleus of some of the opium alkaloids (p. 565). It resembles quinolin in its properties. F. p. 23° ; b. p. 240.5° .

Hydroquinolins.—Compounds corresponding to dihydroquinolins are known. **Tetrahydroquinolins** are formed, by hydration of the pyridin ring, by the action of nascent hydrogen on quinolins. **Decahydroquinolin**, $\text{C}_9\text{H}_{18}\text{N}$, corresponding to piperidin (p. 519), is formed by heating quinolin with hydriodic acid and phosphorus.

Higher Condensed Heterocyclic Compounds—Acridin— $\text{C}_{13}\text{H}_9\text{N}$ (p. 538)—a three-ringed heterocyclic compound, exists in coal tar. It and its homologues are produced by heating acidyl derivatives of diphenylamin with ZnCl_2 . Other three- and four-ringed compounds are produced by condensation of aldehydes with naphthylamin and anthramin, as quinolin is produced from anilin. **Naphthalinolin** is a four-ringed nucleus of two benzene rings fused upon one of naphthdrin (p. 538).

C. PHENYL-PYRIDYL, DIPYRIDYL, AND PYRIDYL-PYRROLE COMPOUNDS.

These compounds (p. 508) contain two nuclei, one at least heterocyclic, united together by loss of two hydrogen atoms.

Phenyl-pyridyls, or **phenyl-pyridins** (p. 519) consist of one or more phenyl groups substituted in pyridin, γ -**Phenyl-pyridyl**, $\text{N} \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CH}-\text{CH} \end{smallmatrix} \text{C}-\text{C} \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CH}-\text{CH} \end{smallmatrix} \text{CH}$, as well as the α and β compounds, and **diphenyl-** and **tetraphenyl-pyridins**, are known.

γ, γ -**Dipyridyl**— $\text{N} \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CH}-\text{CH} \end{smallmatrix} \text{C}-\text{C} \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CH}-\text{CH} \end{smallmatrix} \text{N}$ —is formed by the action of sodium upon pyridin. It forms colorless needles; f. p. 114° ; which yield isonicotinic acid (p. 519) on oxidation. The α - β and β - β dipyridyls are formed by oxidation of the phenanthrolins, and both yield nicotinic acid on oxidation. A fourth, probably α - α , is formed by passing vapor of pyridin through a red-hot tube. The dipyridyls take up nascent hydrogen to form substances, $\text{C}_{10}\text{H}_{14}\text{N}_2$, isomeric with nicotin, and resembling that alkaloid (p. 551) closely in chemical properties and in physiological action. The one obtained from β - β dipyridyl is a very soluble and highly poisonous liquid, called **nicotidin**. That from γ - γ dipyridyl is a crystalline solid, soluble in water, less actively poisonous than nicotin, and called **isonicotin**.

The **pyridyl-pyrroles** are formed by union of a pyridin and a **pyrrole** ring, as the dipyridins are formed by union of two pyridin rings. α -**Pyridin- β -pyrrole**, $\text{HC} \begin{smallmatrix} \text{CH}=\text{CH} \\ \text{CH}-\text{N} \end{smallmatrix} \text{C}-\text{C} \begin{smallmatrix} \text{CH}-\text{NH} \\ \text{CH}=\text{CH} \end{smallmatrix}$, constitutes the nucleus of nicotin (p. 551). It is a crystalline solid; f. p. 72° .

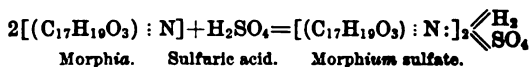
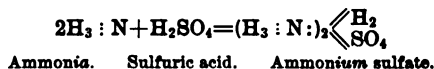
ALKALOIDS.

Until the constitution of all the substances grouped under this term shall have been determined, the limitations of the application of the name can be only provisional. It was first applied to the few alkali-like substances first obtained from vegetable products, the vegetable bases morphin, narcotin, veratrin, strychnin. Afterwards its application was extended, and at the same time made more precise, to include organic, nitrogenized substances, alkaline in reaction, and capable of combining with acids to form salts in the same way as does ammonia. This limitation is, however, too broad, as it classes the aliphatic amins, and other similar bodies, with the true alkaloids, which are cyclic. All substances generally classed as alkaloids, whose

constitution has been determined, contain at least one nitrogen-containing heterocyclic ring, except theobromin and caffein, which are not true alkaloids, but purin bases (p. 533). Almost all alkaloids of known constitution contain the pyridin ring, more or less modified by hydrogenation, either alone or in quinolin or isoquinolin. Therefore, until recently, alkaloids were considered to be: basic substances containing the pyridin ring. But the hygrins, alkaloids existing in coca leaves, are derivatives, not of pyridin, but of pyrrolidin (p. 511), a five-membered nucleus. So far as is now known, no alkaloid contains more than one nitrogen atom in one and the same ring. Therefore, provisionally, it may be stated that the alkaloids are basic substances derived from heterocyclic nuclei containing but one nitrogen atom in any nucleus. Under this definition pyridin and quinolin and their homologues are alkaloids, as well as indole, and other basic pyrrole compounds.

Some of the alkaloids, nicotin, coniïn, sparteïn and arecolin are liquid, volatile, and contain C, N and H. Most of them, to the number of more than a hundred, are solid, crystalline, only partially volatile without decomposition, if at all, and contain C, N, H and O. Most of the alkaloids are very sparingly soluble in water, although some are readily soluble; but soluble in alcohol, ether, petroleum-ether, chloroform, benzene or amylic alcohol. Their salts, on the other hand, are, for the most part, soluble in water, but insoluble in the other solvents mentioned, except alcohol, in which they are soluble. They are laevogyrous, except quinidin, cinchonin, coniïn, narcotin and pilocarpin, which are dextrogyrous. Usually their rotary power is diminished by combination with acids, although with quinin the reverse is the case. Free narcotin is laevogyrous, its salts are dextrogyrous. Most of the alkaloids are bitter in taste, and alkaline in reaction.

The naming of the salts of the alkaloids has been the subject of no little discussion. In obedience to the rules of orthography adopted (see Appendix) the names of the alkaloids are made to terminate in *in*, although in non-chemical writings the termination *ine* is still usual, and the older termination *ia* is occasionally met with. As most of the alkaloids are tertiary amins and some secondary amins, they combine with acids in the same manner that ammonia does, that is, without elimination of water or of hydrogen, and by change of the nitrogen valence from trivalent to quinquivalent:



Therefore these salts do not contain morphin, $C_{17}H_{19}O_3N'''$, as a substitute for the hydrogen of the acid, but the hypothetical morphium ($C_{17}H_{20}O_3N''$), as the ammoniacal salts are not salts of ammonia, NH_3 , but of ammonium, NH_4 . The compounds formed by the union of morphin and other alkaloids with the hydracids, HCl , HBr , HI , may properly and conveniently be referred to as morphin hydrochlorid (not hydrochlorate) hydrobromid, hydroiodid, etc., they being considered, not as salts of those acids, but as compounds in which one of the valences of the quinquivalent nitrogen atom is satisfied by hydrogen and another by chlorin.

Many of the alkaloids behave like esters, and are hydrolyzed by baryta or the caustic alkalies, or by mineral acids, into two components, one a base, the other an acid, the latter usually cyclic and nitrogenous. On the other hand, concentrated HCl removes H_2O from those alkaloids containing more than one hydroxyl, converting them into apo-alkaloids, as morphin is converted into apomorphin. Other alkaloids, containing methoxyl groups (OCH_3), when acted upon by concentrated HCl , are modified by replacement of OH for the methoxyl groups. Reducing agents with alkaloids whose nuclei contain double bonds, form hydro-bases, as piperidin is derived from pyridin. Distillation with zinc-dust causes removal of the lateral chains from the oxygen-containing alkaloids, with liberation of pyridin or quinolin. Oxidizing agents form carboxylic acids, or decompose the alkaloid into an acid and a base, or cause the union of two molecules of the alkaloid with loss of hydrogen.

Separation of Alkaloids from Organic Mixtures.—The separation of an alkaloid from an organic mixture (contents of stomach, viscera, etc.) in a condition of purity sufficient to permit of its identification, is one of the most difficult tasks of the toxicologist, and not to be attempted in a case liable to be the subject of legal inquiry except by one thoroughly competent. The processes usually followed are modifications of that originally used by Stas, of which the most exhaustive is the method of Dragendorff. They depend upon differences in the solubilities of the several alkaloids and of their salts in water or alcohol, and in various solvents immiscible with water. The alkaloid is first extracted as a tartrate, sulfate or hydrochlorid by water or alcohol, acidulated with the appropriate acid, and the extract purified to a clear, acid, watery solution. This acid solution is then successively shaken with the immiscible solvents, such as ether, petroleum-ether, benzene, chloroform, amyl alcohol and acetic ether, the solvents being separated from the aqueous solution, and each evaporated by itself. During this treatment the alkaloids are held in the aqueous solution, while the other solvents extract impurities and certain glucosidal and acid poisons. The watery solution is now

rendered alkaline, which causes liberation of the alkaloid from its saline combination, and is again successively agitated with the immiscible solvents named, they being each individually separated from the aqueous liquid and evaporated. Each solvent extracts those alkaloids which it is capable of dissolving, and they are sought for by the suitable tests in the appropriate residues. Thus strychnin is extracted by benzene, and morphin by amylic alcohol. The details of the process, which are quite elaborate, must be carefully observed, and the student is referred to special treatises upon the subject.

General Reactions of the Alkaloids.—A great number of "general reagents" for alkaloids have been suggested, of which only the more important can be here mentioned:

Potash, soda, ammonia, lime, baryta and *magnesia* precipitate the alkaloids from solutions of their salts.

Phosphomolybdic acid forms a precipitate which is bright-yellow with anilin, morphin, veratrin, aconitin, emetin, atropin, hyoseyamin, theïn, theobromin, coniïn and nicotin; brownish-yellow with narcotin, codeïn, and piperin; yellowish-white with quinin, cinchonin and strychnin; yolk-yellow with brucin (DeVry's, or Sonnenschein's reagent).

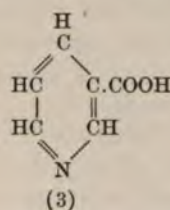
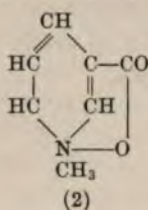
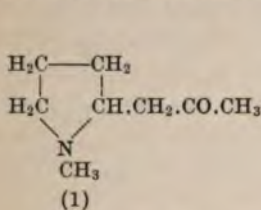
Potassium iodhydrargyrate gives a yellowish precipitate with alkaloidal solutions which are acid, neutral or faintly alkaline in reaction (Mayer's reagent).

Classification of the Alkaloids.—The alkaloids of known, or partially known constitution, can be classified according to the nuclei which they contain:

- A. *Pyrrolidin Alkaloids*.—The hygrins.
 - B. *Pyridin Alkaloids*.—Trigonellin, pilocarpin (?).
 - C. *Piperideïn (tetrahydropyridin) Alkaloids*.—Arecolin, arecaïdin, γ -coniceïn (?), pseudopelletierin, pelletierin (?).
 - D. *Piperidin Alkaloids*.—Coniïn, conhydrin, arecaïn, juvacin, piperin.
 - E. *Pyrrolidin-pyridin Alkaloids*.—Nicotin.
 - F. *Pyrrolidin-piperidin Alkaloids*.—*Tropan Alkaloids*.—Atropin, hyoseyamin, hyoscin (?), ecgonin, cocaïn, cinnamyl-cocaïn, α -truxillin, β -truxillin, benzoyl-ecgonin, tropacocaïn.
 - G. *Quinolin Alkaloids*.—Cinchona alkaloids, strychnos alkaloids (?).
 - H. *Isoquinolin Alkaloids*.—Papaverin, narcotin, narceïn (?), hydrastin, berberin (?).
 - I. *Phenanthrene Alkaloids*.—Morphin, codeïn, thebaïn.
 - X. Alkaloids of unknown constitution.
- Pyrrolidin Alkaloids*.—**Hygrin**, $C_8H_{15}NO$, and **Cuzcohygrin**, $C_{12}H_{24}N_2O$, are poisonous alkaloids, occurring in the leaves of *Erythroxyl-*

lon coca. The former is 1-methyl-2-acetonylpyrrolidin (1, below), and the latter is derived from it by the substitution of another pyrrolidin ring for H in CH₃, and is therefore sym. di-1-methylpyrrolidyl acetone.

Pyridin Alkaloids.—**Trigonellin**, C₇H₇NO₂ (2, below), a non-poisonous, crystalline alkaloid, which occurs in fenugreek, peas and hemp, is identical with the synthetic methyl betain (p. 384) of nicotinic, or pyridin-β-monocarboxylic acid (3):



The jaborandi alkaloids, **pilocarpin**, C₁₁H₁₆N₂O₂, **pilocarpidin**, C₁₀H₁₄N₂O₂, and **jaborin**, C₂₂H₃₂N₄O₄, probably belong in this group.

Piperidein Alkaloids.—**Arecaidin**, C₇H₁₁NO₂, one of the four alkaloids of the betel-nut, is the β-monocarboxylic acid of *n*-methyl-tetrahydropyridin; and **arecolin**, C₈H₁₃NO₂, another alkaloid from the same plant, is its methyl ester.

Of the four alkaloids from pomegranate—**pelletierin**, C₈H₁₅NO, **isopelletierin**, C₈H₁₅NO, **methylpelletierin**, C₉H₁₇NO, and **pseudopelletierin**, C₉H₁₅NO,—the only one whose constitution is known is the last named, which is *n*-methyl-2-acetonyltetrahydropyridin.

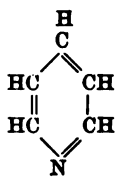
Piperidin Alkaloids.—The alkaloids known to contain a single piperidin ring as a nucleus are the five alkaloids of *Conium maculatum*, **coniin**, C₈H₁₇N, **conhydrin**, C₈H₁₇NO, **conicein**, C₈H₁₅N, ***n*-methylconiin**, C₉H₁₉N, and **pseudoconhydrin**, C₈H₁₇NO; and two of the four betel-nut alkaloids: **arecaïn**, C₇H₁₁NO₂, and **guvacin**, C₆H₉NO₂.

Coniïn—C₈H₁₇N—is one of the most simply constituted of the natural vegetable alkaloids, and was the first to be produced synthetically. It is a colorless, oily liquid; has an acrid taste and a disagreeable, penetrating odor; sp.gr. 0.844; can be distilled when protected from air; b.p. 166°. Exposed to air it resinifies. The natural alkaloid is *d*-coniïn, [*a*]_D=15.7°. It is very sparingly soluble in water, but is more soluble in cold than in hot water; soluble in all proportions in alcohol, easily soluble in ether, and in fixed and volatile oils.

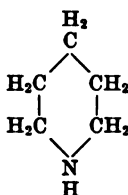
Its vapor at ordinary temperatures forms a white cloud when in contact with a glass rod moistened with HCl, as does NH₃. It forms salts which crystallize with difficulty. Chlorin and bromin combine with it to form crystallizable compounds; iodin in alcoholic solution

forms a brown precipitate in alcoholic solutions of coniïn, which is soluble without color in an excess. Ethyl and methyl iodids combine with it to form crystallizable compounds; iodine in alcoholic solution forms a brown precipitate in alcoholic solutions of coniïn, which is soluble without color in an excess. Ethyl and methyl iodids combine with it to form ethyl- and methyl-coniïn hydriodids.

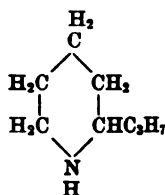
It has been obtained synthetically from α -picolin by reactions which show it to be α -propyl piperidin. The relations of pyridin, piperidin, and coniïn are shown by the following formulæ:



Pyridin.



Piperidin.

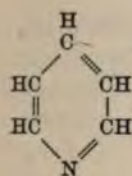


Coniïn.

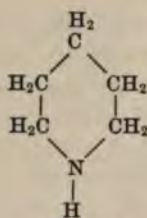
ANALYTICAL CHARACTERS.—(1.) With dry HCl gas it turns red-dish-purple, and then dark-blue. (2) Aqueous HCl of sp. gr. 1.12 evaporated from coniïn leaves a green-blue, crystalline mass. (3) With iodic acid: a white ppt. from alcoholic solutions. (4) With H_2SO_4 and evaporation of the acid: a red color, changing to green, and an odor of butyric acid. (5) When mixed with commercial nitrobenzene a fine blue color is produced, changing to red and yellow.

Paraconiïn— $\text{C}_8\text{H}_{15}\text{N}$ —is a synthetical product closely resembling coniïn, obtained by first allowing butyric aldehyde and an alcoholic solution of ammonia to remain some months in contact at 30° (86° F.), when dibutyraldin is formed: $2(\text{C}_4\text{H}_8\text{O}) + \text{NH}_3 = \text{C}_8\text{H}_{17}\text{NO} + \text{H}_2\text{O}$. The dibutyraldin thus obtained is then heated under pressure to 150° – 180° (302° – 356° F.), when it loses water, and forms paraconiïn: $\text{C}_8\text{H}_{17}\text{NO} = \text{C}_8\text{H}_{15}\text{N} + \text{H}_2\text{O}$. A synthesis which, in connection with the decompositions of paraconiïn, shows its rational formula to be $\begin{array}{c} (\text{C}_4\text{H}_7)_2 \\ \diagup \quad \diagdown \\ \text{H} \quad \text{N} \end{array}$.

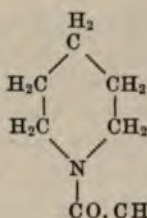
Piperin— $\text{C}_{17}\text{H}_{19}\text{NO}_3$ —isomeric with morphin, and occurring in black and white pepper, crystallizes in large prisms; f. p. 128° ; almost insoluble in water, readily soluble in alcohol and in ether. It is a weak base, without alkaline reaction, and only forming very unstable salts with concentrated acids. It is one of the alkaloids whose complete synthesis has been accomplished, and is quite directly derived from piperidin, of which it is an n -acydyl derivative. When piperin is heated with alcoholic soda, it is hydrolysed into piperic acid, $\text{C}_{12}\text{H}_{10}\text{O}_4$ (p. 458), and piperidin. It is therefore piperidin piperate, or piperidin-3, 4-methylene-dioxy-cinnamyl-acrylate:



Pyridin.



Piperidin.

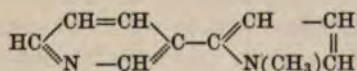


Piperin.

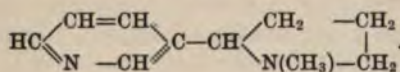
Pyrrolidin-pyridin Alkaloids are represented by

Nicotin— $C_{10}H_{14}N_2$ —which exists in tobacco in the proportion of 2-8 per cent. It is a colorless, oily liquid, which turns brown on exposure to air, has a burning, caustic taste, and a disagreeable, penetrating odor. It distils at 250° (392° F.); burns with a luminous flame; sp. gr. 1.027 at 15° (59° F.); is very soluble in water, alcohol, the fatty oils, and ether. The last-named fluid removes it from its aqueous solution when the two are shaken together. It absorbs water rapidly from moist air. Its salts are deliquescent, and crystallize with difficulty. The natural alkaloid is 1-nicotin. The i-nicotin has been obtained by total synthesis, through β -amidopyridin. From this 1-nicotin is produced by the action of tartaric acid.

The oxidation of nicotin produces nicotinic, or β monocarbopyridic, acid (p. 519). When distilled with zinc chlorid and lime it yields pyrrole, ammonia, methylamin, hydrogen, and pyridin bases. When heated to 250° (482° F.) it yields a collidin along with other products. By limited oxidation it produces a substance, $C_{10}H_{10}N_2$, formerly considered as isodipyridin, but shown to be β -pyridin-n-methyl-a-pyrrole,



of which nicotin is the tetrahydro, or pyrrolidin derivative—

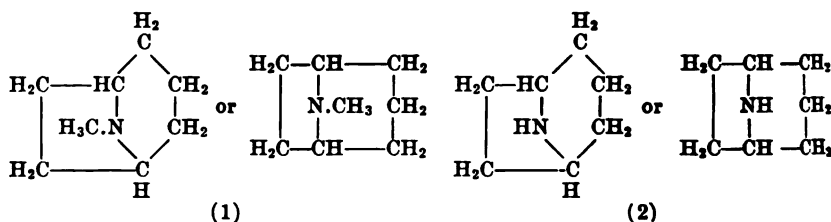


ANALYTICAL CHARACTERS.—(1) Its ethereal solution, added to an ethereal solution of iodine, separates a reddish-brown, resinoid oil, which gradually becomes crystalline. (2) With HCl, a violet color. (3) With HNO_3 , an orange color.

TOXICOLOGY.—Nicotin is a very active poison. The free alkaloid is probably capable of causing death in doses of two to three drops. It was the first alkaloid to be separated from the cadaver in a case of homicide. Most cases of poisoning from nicotin are due to tobacco, frequently resulting from its use in enemata. When administered to

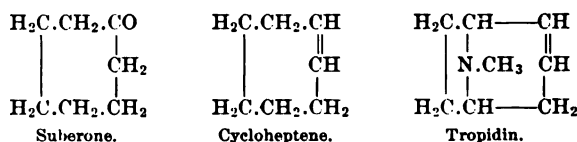
dogs in doses of two to four drops, its effects begin within half a minute to two minutes, and death ensues within one to five minutes. In man tobacco or its decoction causes nausea, vertigo, dilatation of the pupils, vomiting, syncope, diminution of the rapidity and force of the heart. With large doses there are no subjective symptoms, the victim falls unconscious instantly, and dies within five minutes, without convulsions, and with very few or only one deep sighing respiratory act. The l-nicotin has double the toxic power of d-nicotin, and the two forms differ in the nature of the action produced.

Pyrrolidin-piperidin Alkaloids—Tropan Alkaloids.—The alkaloids of this group, most of which are ester-alkaloids, including the atropic alkaloids, atropin, hyoscyamin, and hyoscin, and the coca alkaloids, ecgonin, cocaïn, cinnamyl-cocaïn, α - and β -truxillins, benzoylecgonin and tropacocaïn, are derivatives of tropan (1), the n -methyl derivative of nortropan (2), both of which are known, as well as many of their compounds other than alkaloids:



Nortropan may be considered as formed by condensation of a pyrrolidin ring and a piperidin ring, having the group $=\text{CH}\cdot\text{NH}\cdot\text{CH}=\text{}$ in common. The following tropan derivatives are of interest in connection with the syntheses of atropic and coca alkaloids.

Tropidin—(formula below)—is a dehydrotropan, first obtained as a product of decomposition of atropin, and later of cocaïn, thus indicating the relationship of the two alkaloids. It has been obtained by total synthesis, starting from synthetic glycerol (p. 296), through allyl bromid (p. 426), trimethylene bromid, trimethylene cyanid, glutaric acid (p. 337), to suberone (formula below). From suberone to tropidin many steps are required, the principal intermediate products being cycloheptene (2), cycloheptatriène, and α -methyltropidin:



Tropan—(formula p. 553)—**4-Tropan Alcohol**—is formed, through its space isomere, ψ -tropan, by conversion of tropidin into a dibromo

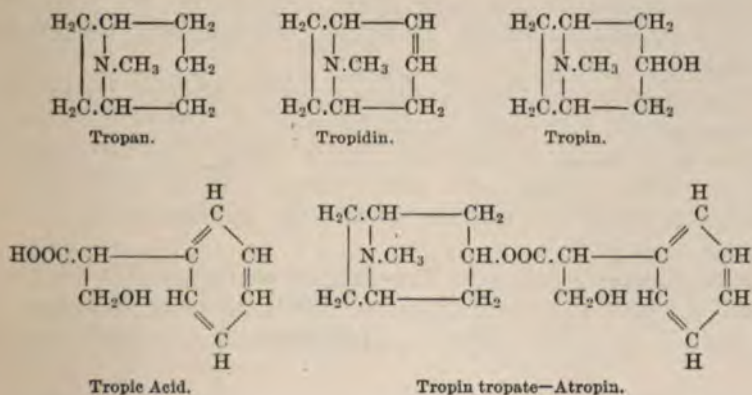
addition product, and splitting off of Br_2 and addition of H_2O by heating with H_2SO_4 at 200° . Tropin is the alcoholic component of atropin, hyoscyamin and the tropeïns, and of which ecgonin (p. 556) is the carboxylic acid.

Atropin—i-Tropin tropate— $\text{C}_{17}\text{H}_{23}\text{NO}_3$.—Belladonna, stramonium, hyoscyamus and duboisia contain five alkaloids: atropin, hyoscyamin, hyoscin, scopolamin and belladonnin; of which the first two are optical isomeres of each other.

Atropin forms colorless, silky needles, sparingly soluble in cold water, more readily in hot water, very soluble in chloroform. It is odorless, has a disagreeable, persistent, bitter taste. Both tropin and tropic acid (see below) contain an asymmetric carbon atom. The tropin in atropin is i-tropin, and the acid is d-tropic acid. Both natural and synthetic atropins are optically inactive. Atropin is distinctly alkaline, and neutralizes acids with formation of salts. The sulfate is a white, crystalline powder, readily soluble in water.

Atropin is the type of the "ester alkaloids" saponifiable into an acid and an alcoholic component. When it is acted upon by BaH_2O_2 at 60° , or by NaHO or HCl at 120° – 130° , it is saponified, after the manner of an ester, into tropic, or α -phenylhydraacrylic acid (p. 463), $\text{C}_6\text{H}_5.\text{CH} \begin{smallmatrix} \text{COOH} \\ \text{CH}_2\text{OH} \end{smallmatrix}$, and a secondary cyclic alcohol, tropin (formula below). But if the action be prolonged the tropic acid is further decomposed into α -phenylacrylic, or atropic, and isatropic acids (p. 457). And if, during the action of HCl , the temperature rises to 180° , the tropin loses water, and is converted into tropidin.

The total synthesis of atropin has been accomplished; the tropin component having been obtained in the manner indicated on p. 552, and tropic acid by the synthesis described on p. 463. Tropin and tropic acid readily combine to form atropin: $\text{C}_8\text{H}_{15}\text{NO} + \text{C}_9\text{H}_{10}\text{O}_3 = \text{C}_{17}\text{H}_{23}\text{NO}_3 + \text{H}_2\text{O}$. The relation of atropin to its progenitors is shown in the following formulæ:



ANALYTICAL CHARACTERS.—(1) If a fragment of potassium dichromate be dissolved in a few drops of H_2SO_4 , the mixture warmed, a fragment of atropin and a drop or two of H_2O added, and the mixture stirred, an odor of orange-blossoms is developed. (2) A solution of atropin dropped upon the eye of a cat produces dilatation of the pupil. (3) The dry alkaloid (or salt) is moistened with fuming HNO_3 and the mixture dried on the water-bath. When cold, it is moistened with an alcoholic solution of KHO : a violet color, which changes to red (Vitali). (4) If a saturated solution of Br in HBr be added to a solution of atropin, a yellow precipitate is formed, which rapidly becomes crystalline, and which is insoluble in acetic acid, sparingly soluble in H_2SO_4 and HCl .

TOXICOLOGY.—The clinical history of atropic poisoning is divisible into two stages, the first one of delirium, in which the prominent symptoms are dryness of the throat, thirst, difficulty of deglutition and spasms upon swallowing liquids, face at first pale, afterwards highly reddened, pulse extremely rapid, eyes prominent, brilliant, with widely-dilated pupils, complete paralysis of accommodation, disturbances of vision, attacks of giddiness and vertigo, with severe headache, followed by delirium, occasionally silent or muttering, but usually violent, noisy and destructive, accompanied by the most fantastic delusions and hallucinations. Usually the urine is retained, and the body temperature is above the normal. The delirium gradually subsides, and the second stage, that of coma, is established, with slow, stertorous respiration, and gradually failing pulse, until death occurs from respiratory or cardiac paralysis, or sometimes in an attack of syncope during apparent amelioration. In some cases, the patient rapidly becomes comatose at the outset, and the symptoms of the first stage are manifested as the coma diminishes. The treatment should consist of lavage of the stomach, and morphin may be given cautiously during the period of violent excitement. In the second stage, the treatment is the same as in morphin poisoning. Pilocarpin may be given, in not too large doses, to stimulate the secretion of saliva. Atropic poisoning leaves no characteristic post-mortem lesions.

Hyoscyamin— $\text{C}_{17}\text{H}_{23}\text{NO}_3$ —isomeric with atropin, predominates in *Hyoscyamus niger*, and in *mandragora*. It differs from atropin principally in being lævogyrous, $[\alpha]_D = -20.3^\circ$, and on saponification it yields l-tropic acid and i-tropin. It is converted into atropin very easily, by heat, or by addition of alkali to its alcoholic solution.

Apoatropin—*Atropamin*—**Tropin atropate**— $\text{C}_{17}\text{H}_{21}\text{NO}_2$ —is formed by the action of dehydrating agents, H_2SO_4 , P_2O_5 , etc., on atropin or hyoscyamin, by splitting off of H_2O from the acid component, thus con-

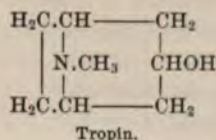
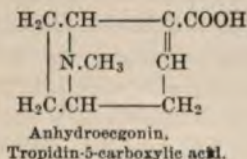
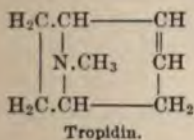
verting the residue of the saturated tropic acid into that of the unsaturated atropic acid. By heat it is converted into its isomere, **belladonnin**, an alkaloid which accompanies atropin in belladonna. **Hyoscin** and **scopolamin**, $C_{17}H_{21}NO_4$, are two isomeric, mydriatic alkaloids, accompanying atropin in belladonna. The latter on decomposition yields tropic acid and **scopolin**, $C_8H_{13}NO_2$, which is closely related to tropin, $C_8H_{15}NO$.

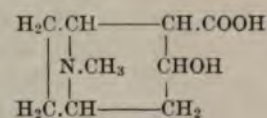
Tropeïns—are ester-like derivatives of tropin with acids, similar to atropin. Many such have been formed with organic acids, benzoic, salicylic, etc. That formed with mandelic acid (p. 463) is known as **homatropin**, $C_8H_{14}N.OOC.CH(OH).C_6H_5$, and is used as a mydriatic having a less prolonged action than atropin. Only those tropeïns whose acid radicals contain an alcoholic hydroxyl have a mydriatic action.

Ecgonin— $C_9H_{15}NO_3$ —an alkaloid existing in *Erythroxylon coca*, and the parent substance of cocaïn and other coca alkaloids, is 4-oxy-tropan-5-monocarboxylic acid (p. 556). By the action of dehydrating agents upon ecgonin the alcoholic OH and an H atom are split off, and **anhydroecgonin**, $C_9H_{13}NO_2$, is formed, which, by splitting off of CO_2 from the carboxyl, forms tropidin. Ecgonin, being both basic and acid, forms esters and salts, and numerous products of derivation other than cocaïn. When acted upon by a mixture of methyl iodid and benzoic anhydrid, ecgonin is converted into cocaïn. Or by substitution of other alkyl iodids for that of methyl, other alkaloids, homologous with cocaïn, are obtained (see formulæ below).

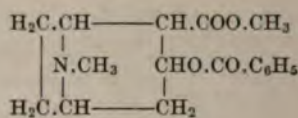
Cocaïn— $C_{17}H_{21}NO_4$ —the most important of the coca alkaloids, is closely related chemically to atropin. It crystallizes in large four- or six-sided prisms; f. p. 98° ; sparingly soluble in water, readily soluble in alcohol, ether and chloroform; somewhat bitter at first, but causing paralysis of the sense of taste afterwards; strongly alkaline. Its hydrochlorid, used as a local anæsthetic, crystallizes in prismatic needles, readily soluble in water.

When boiled with water, cocaïn is hydrolysed into **benzoylecgonin**, $C_{16}H_{19}NO_4$, and methylic alcohol. If the hydrolysis be effected by BaH_2O_2 , or by concentrated mineral acids, it is more complete, and ecgonin, benzoic acid and methylic alcohol are formed. Cocaïn is, therefore, the methyl ester of benzoylecgonin, and ecgonin is tropan-5-monocarboxylic acid:





Egonin.
Tropin-5-carboxylic acid.



Cocain.
Methyl benzoylegonate.

ANALYTICAL CHARACTERS.—(1) Picric acid forms a yellow ppt. in concentrated solutions. (2) A solution of iodine in KI solution gives a fine red precipitate in a solution containing 1 to 10,000 of cocaine. (3) When cocaine hydrochloride is heated with concentrated H_2SO_4 until white fumes are given off abundantly, and potassium iodate is added to the still hot liquid, abundant violet vapors are given off, and the liquid becomes deep red-violet, changing to brilliant green, then to pink, and finally to pure blue-violet. (4) Potassium permanganate produces a violet, crystalline ppt. (5) A 5 per cent. solution of chromic acid produces an orange-colored ppt., which immediately redissolves, but, after addition of HCl, remains permanent. (6) If cocaine hydrochloride be mixed dry with Hg_2Cl_2 , the white mixture in moist air turns gray or black. Pilocarpin gives the same reaction.

Pilocarpin— $\text{C}_{11}\text{H}_{16}\text{N}_2\text{O}_2$ —occurs in jaborandi, along with two other alkaloids, jaborin, $\text{C}_{22}\text{H}_{32}\text{N}_4\text{O}_4(?)$, and pilocarpidin, $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_2$, and an essential oil, consisting principally of pilocarpene, $\text{C}_{10}\text{H}_{16}$. It is colorless, crystalline, readily soluble in water, alcohol, ether and chloroform. It is converted by heat into jaborin; and by HNO_3 or HCl into a mixture of jaborin and jaborandin, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$. Like piperin, atropin, cocaine, etc., it is ethereal in character and is decomposed into CO_2 , methylamin, butyric acid, and pyridin bases by KHO or NaHO. When oxidized by potassium permanganate it yields pyridin-tartronic acid, $\text{C}_5\text{H}_4\text{N} \cdot \text{C} : (\text{OH})(\text{COOH})_2$, and this, on further oxidation, nicotinic acid, $\text{C}_5\text{H}_4\text{N} \cdot \text{COOH}$. When its hydrochloride is heated to 200° , in presence of H_2O , it takes up water and is decomposed into pilocarpidin and methylic alcohol. Conversely, pilocarpin is produced by the action of methyl iodide upon pilocarpidin. Although the constitution of pilocarpin is not established, the above and other reactions indicate that it contains the pyridin ring, to which the cyclic group, $\text{C}_6\text{H}_{12}\text{NO}_2$, is attached in the β position; and that it is methyl-pilocarpidin.

Quinolin Alkaloids—Cinchona Alkaloids.—Although by no means so complex a substance as opium, cinchona bark contains a great number of substances: *quinin*, *cinchonin*, *quinidin*, *cinchonidin*, *aricin*; *quinic*, *quinotannic* and *quinovic acids*; *cinchona-red*, etc. Of these the most important are quinin and cinchonin.

Quinin—Quinina (U. S.)— $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2 + n \text{ Aq} - 324 + n18$ —exists in the bark of a variety of trees of the genera *Cinchona* and *China*,

which vary considerably in their richness in this alkaloid. The best samples of calisaya bark contain from 30 to 32 parts per 1,000 of the sulfate; the intermediate grades 4 to 20 parts per 1,000; inferior grades of bark contain from mere traces to 6 parts per 1,000.

It is known in three different states of hydration, with 1, 2, and 3 Aq, and anhydrous. The anhydrous form is an amorphous, resinous substance, obtained by evaporation of solutions in anhydrous alcohol or ether. The first hydrate is obtained in crystals by exposing to air recently precipitated and well-washed quinin. The second by precipitating by ammonia a solution of quinin sulfate, in which H has been previously liberated by the action of Zn upon H_2SO_4 ; it is a greenish, resinous body, which loses H_2O at 150° (302°F.). The third, that to which the following remarks apply, is formed by precipitating solutions of quinin salts with ammonia.

It crystallizes in hexagonal prisms; very bitter; fuses at 57° (134.6°F.); loses 1 Aq at 100° (212°F.), and the remainder at 125° (257°F.); becomes colored, swells up, and, finally, burns with a smoky flame. It does not sublime. It dissolves in 2,200 pts. of cold water, in 763 of hot water, very soluble in alcohol and chloroform; soluble in amyl alcohol, benzene, fatty and essential oils, and ether. Its alcoholic solution is powerfully lævogyrous, $[\alpha]_D = -270.7^\circ$ at 18° (64.4°F.), which is diminished by increase of temperature, but increased by the presence of acids.

ANALYTICAL CHARACTERS.—(1) Dilute H_2SO_4 dissolves quinin in colorless but fluorescent solution (see below). (2) Solutions of quinin salts turn green when treated with chlorin-water and then with ammonium hydroxid. (3) Chlorin passed through water holding quinin in suspension forms a red solution. (4) Solution of quinin treated with chlorin-water and then with fragments of potassium ferrocyanid becomes pink, passing to red.

SULFATE—*Disulfate*—*Quininæ sulfas* (U. S.)—*Quiniæ sulfas* (Br.)— $\text{SO}_4(\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_2)_2 + 7\text{Aq} - 746 + 126$ —crystallizes in prismatic needles; very light; intensely bitter; phosphorescent at 100° (212°F.); fuses readily; loses its Aq at 120° (248°F.), turns red, and finally carbonizes; effloresces in air, losing 6 Aq; soluble in 740 pts. of water at 13° (55.4°F.), in 30 pts. of boiling water, and 60 pts. of alcohol. Its solution with alcoholic solution of iodine deposits brilliant green crystals of *iodoquinin sulfate*.

HYDROSULFATE—*Quininæ bisulfas* (U. S.)— $\text{SO}_4\text{H}(\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_2) + 7\text{Aq} - 422 + 126$ —is formed when the sulfate is dissolved in excess of dilute H_2SO_4 . It crystallizes in long, silky needles, or in short, rectangular prisms; soluble in 10 pts. of water at 15° (59°F.). Its solutions exhibit a marked fluorescence, being colorless, but showing a

fine pale-blue color when illuminated by a bright light against a dark background.

By the action of alkaline hydroxids upon quinin, formic acid, quinolin (p. 543), and pyridin bases (p. 517) are produced.

Concentrated HCl at 140° – 150° (284° – 302° F.) decomposes quinin with separation of methyl chlorid and formation of **apoquinin**, $C_{19}H_{22}N_2O_2$, an amorphous base.

Oxidizing agents produce from quinin oxalic acid and pyridin carboxylic acids, notably **pyridin-2,3-dicarboxylic**, or **cinchomeronic acid**, $C_5H_3N(COOH)_2$, which are also formed by oxidation of cinchonin.

Although cinchonin differs from quinin in composition by CH_2O , and although the decompositions of the two bases show them both to be related to the quinolin and pyridin bases, attempts to convert cinchonin into quinin have resulted only in the formation of other products, among which is an isomere of quinin, **oxycinchonin**.

Methylquinin, $C_{20}H_{24}N_2O_2CH_3$, is a base which has a curare-like action.

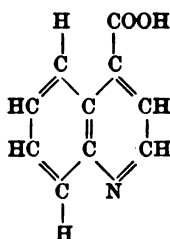
Cinchonin—Cinchonina (U. S.)— $C_{19}H_{22}N_2O$ —294—occurs in Peruvian bark to the amount of from 2 to 30 pts. per 1,000. It crystallizes without Aq in colorless prisms; fuses at 150° (302° F.); soluble in 3,810 pts. of water at 10° (50° F.), in 2,500 pts. of boiling water; in 140 parts of alcohol, and in 40 pts. of chloroform. The salts of cinchonin resemble those of quinin in composition; are quite soluble in water and in alcohol; are not fluorescent; are permanent in air; and are phosphorescent at 100° (212° F.).

Quinidin and Quinicin—are bases isomeric with quinin; the former occurring in cinchona bark, and distinguishable from quinin by its strong dextrorotary power; the second a product of the action of heat on quinin, not existing in cinchona.

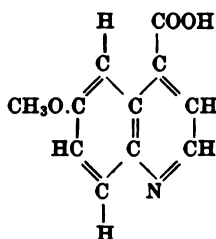
Cinchonidin—a base, isomeric with cinchonin, occurring in certain varieties of bark; lævogyrous. At 130° (266° F.), H_2SO_4 converts it into another isomere, **cinchoninicin**.

Constitution of Cinchona Alkaloids—The constitution of no cinchona alkaloid has yet been completely determined. Enough has, however, been ascertained to show that cinchonin and quinin contain a quinolin nucleus, united to another cyclic nucleus, containing the second N atom, and which is probably a modified piperidin. The difference between the empirical formulæ of cinchonin, $C_{19}H_{22}N_2O$, and of quinin, $C_{20}H_{24}N_2O_2$, is CH_2O in favor of the latter, which would represent the substitution of methoxyl, CH_3O , for H. When cinchonin and quinin are oxidized by chromic acid they yield two quinolin-carboxylic acids also differing from each other by CH_2O . Cinchonin yields cinchoninic acid, which is known to be γ -quinolin

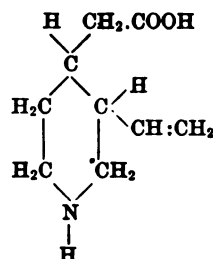
carboxylic acid; while quinin yields quinic acid, which has been shown to be the methyl-phenol ether of p-oxyquinolin- γ -carboxylic acid (see formulæ below). Therefore the group CH_2O , by which cinchonin and quinolin differ, exists in the quinolin ring, and the "second half," or the portion of the molecule other than the quinolin ring, is the same in the two alkaloids. This is further proven by the fact that on decomposition by PCl_5 and subsequent treatment with alcoholic KHO , cinchonin yields lepidin, $\text{C}_{10}\text{H}_9\text{N}$, the next superior homologue of quinolin, $\text{C}_9\text{H}_7\text{N}$, while quinin yields p-methoxy-lepidin, $\text{C}_{10}\text{H}_9(\text{OCH}_3)\text{N}$, and the other product of the decomposition is one and the same substance from either alkaloid, a substance which has been called meroquinene, $\text{C}_9\text{H}_{15}\text{NO}_2$, which on treatment with HgCl_2 and HCl is converted into β -ethyl- γ -methyl-pyridin, and whose probable constitution is expressed by the formula given below. So far as determined, therefore, the formulæ of cinchonin and of quinin are those here given, the arrangement of the group $\text{C}_{10}\text{H}_{15}(\text{OH})\text{N}$ remaining to be determined:



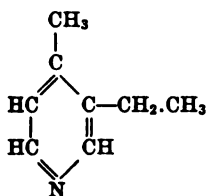
Cinchoninic acid,
(γ -quinolin carboxylic acid).



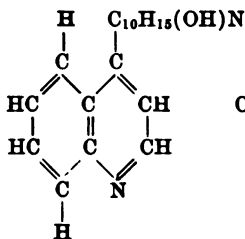
Quinic acid, (3-Methoxyquinolin- γ -carboxylic acid).



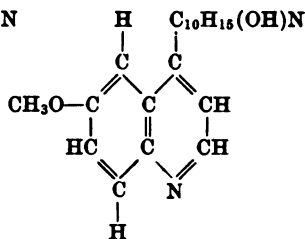
Meroquinene (?)



β -Ethyl- γ -methyl-pyridin.



Cinchonin.



Quinin.

Alkaloids of the Loganiaceæ—Strychnos Alkaloids.—This group includes strychnin and brucin and their alkyl derivatives, and the curare alkaloids.

Strychnin — $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$ —exists in the seeds and bark of different varieties of *Strychnos*, notably *Strychnos nux-vomica*.

It crystallizes on slow evaporation of its solutions in orthorhombic

prisms; very sparingly soluble in water and in strong alcohol; soluble in 5 parts of chloroform. Its aqueous solution is intensely bitter, the taste being perceptible in a solution containing 1 part in 200,000.

It is a powerful base; neutralizes and dissolves in concentrated H_2SO_4 without coloration, and precipitates many metallic oxides from solutions of their salts. Its salts are mostly crystallizable, soluble in water and in alcohol, and intensely bitter. The *acetate* is the most soluble. The *neutral sulfate* crystallizes, with 7 Aq. in rectangular prisms. Methyl and ethyl iodids react with strychnin to produce **methyl** or **ethylstrychnium** iodids, white, crystalline substances, producing an action on the economy similar to that of curare. Heated with fuming HNO_3 , strychnin yields picric acid. Heated with baryta water to 130° , it yields **isostrychnic acid**, $\text{C}_{20}\text{H}_{23}\text{N}_2\text{O}.\text{COOH}$; and when treated with sodium alcoholate, **strychnic acid**, by addition of H_2O . By boiling with concentrated hydriodic acid and red phosphorus it is converted into **desoxystrychnin**, $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}$, which is further reduced by electrolysis to **dihydrostrychnolin**, $\text{C}_{21}\text{H}_{28}\text{N}_2$. Strychnin itself, by electrolysis, forms two bases, **tetrahydro-strychnin**, $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2$, and **strychnidin**, $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}$. But little is known of the constitution of strychnin, which is, however, probably a derivative of tetrahydroquinolin.

ANALYTICAL CHARACTERS.—(1) Dissolves in concentrated H_2SO_4 , without color. The solution deposits strychnin when diluted with water, or when neutralized with magnesia or an alkali. (2) If a fragment of potassium dichromate (or other substance capable of yielding nascent oxygen) be drawn through a solution of strychnin in H_2SO_4 , it is followed by a streak of color; at first blue (very transitory and frequently not observed), then a brilliant violet, which slowly passes to rose-pink, and finally to yellow. Reacts with $\frac{1}{30000}$ grain of strychnin. (3) A dilute solution of potassium dichromate forms a yellow, crystalline ppt. in strychnin solutions, which, when washed and treated with concentrated H_2SO_4 , gives the play of colors indicated in 2. (4) If a solution of strychnin be evaporated on a bit of platinum foil, the residue moistened with concentrated H_2SO_4 , the foil connected with the + pole of a single Grove cell, and a platinum wire from the — pole brought in contact with the surface of the acid, a violet color appears upon the surface of the foil. (5) Strychnin and its salts are intensely bitter. (6) A solution of strychnin introduced under the skin of the back of a frog causes difficulty of respiration and tetanic spasms, which are aggravated by the slightest irritation, and twitching of the muscles during the intervals between the convulsions. With a small frog, $\frac{1}{16000}$ grain of strychnium acetate will produce tetanic spasms in ten minutes. White mice, 14 to 16 days old, are even more susceptible to the action of strychnin than

frogs. (7) Solid strychnin, moistened with a solution of iodic acid in H_2SO_4 , produces a yellow color, changing to brick-red, and then to violet-red. (8) Moderately concentrated HNO_3 colors strychnin yellow in the cold. (9) A warm solution of strychnin in dilute HNO_3 produces a scarlet-red color on addition of a little KClO_3 . A drop or two of ammonia changes this to brown. On evaporation to dryness, a green residue remains, which forms a green solution in water, changes to orange-brown with KHO , and returns to green with HNO_3 .

TOXICOLOGY.—Strychnin produces a sense of suffocation, thirst, tetanic spasms, usually opisthotonos, sometimes emprosthotonos, occasionally vomiting, contraction of the pupils during the spasms, and death, either by asphyxia during a paroxysm, or by exhaustion during a remission. The symptoms appear in from a few minutes to an hour after taking the poison, usually in less than twenty minutes; and death in from five minutes to six hours, usually within two hours. Death has been caused by $\frac{1}{4}$ grain, and recovery has followed the taking of 20 grains.

The treatment should consist in bringing the patient under the influence of chloral hydrate or of chloroform, and then washing out the stomach. The patient should be kept as quiet as possible, as the slightest unexpected irritation will produce a spasm.

Strychnin is one of the most stable of the alkaloids, and may remain for a long time in contact with putrefying organic matter without suffering decomposition.

Brucin — $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_4 + 4\text{Aq}$ — 394 + 72 — accompanies strychnin. It forms oblique rhomboidal prisms, which lose their Aq in dry air. Sparingly soluble in H_2O , readily soluble in alcohol, chloroform, and amyl alcohol; intensely bitter. It is a powerful base and most of its salts are soluble and crystalline. Its action on the economy is similar to that of strychnin, but much less energetic.

ANALYTICAL CHARACTERS.—(1) Concentrated HNO_3 colors it bright red, soon passing to yellow; stannous chlorid, or colorless NH_4HS , changes the red color to violet. (2) Chlorin-water, or Cl , colors brucin bright red, changed to yellowish-brown by NH_4HO .

Curarin — $\text{C}_{36}\text{H}_{35}\text{N}(?)$ — is an alkaloid obtainable from the South American arrow-poison, *curare*, or *woorara*. It crystallizes in four-sided, colorless prisms, which are hygroscopic, faintly alkaline, and intensely bitter.

Curarin dissolves in H_2SO_4 , forming a pale-violet solution, which slowly changes to red. If a crystal of potassium dichromate be drawn through the H_2SO_4 solution, it is followed by a violet coloration, which differs from the similar color obtained with strychnin under similar circumstances, in being more permanent, and in the absence of the following pink and yellow tints.

Isoquinolin and Phinanthrene Alkaloids.—The opium, hydrastis, berberis and corydalis alkaloids are included in these groups. Of the opium alkaloids, papaverin, narcotin and narceïn are certainly derivatives of isoquinolin. Morphin and codeïn, on the other hand, do not contain the isoquinolin nucleus, but a phenanthrene nucleus having a nitrogen-containing ring condensed upon it. But until the constitution of these two alkaloids is established with more completeness it is not desirable to separate them from their congeners (see p. 565).

Opium Alkaloids.—Opium is the dried juice obtained by making incisions in the unripe capsules of the poppy, *Papaver somniferum*. It is of exceeding complex composition, and contains meconic (p. 517), lactic and sulfuric acids, with which the alkaloids are in combination, meconin (p. 462), gum, caoutchouc, wax, sugar, resins, etc., and a number of alkaloids. Some twenty alkaloids have been obtained from opium, but of these several are probably produced by the processes of extraction. The most important of the natural alkaloids and the average percentage in which they exist in opium of good quality are: morphin, 10%; narcotin, 6%; papaverin, 1%; codeïn, 0.3%; narceïn, 0.2%; and thebaïn, 0.15%.

Morphin — Morphina (U. S.)— $C_{17}H_{19}NO_3 + Aq - 285 + 18$ — crystallizes in colorless prisms; odorless, but very bitter; it fuses at 120° , losing its Aq. More strongly heated, it swells up, becomes carbonized, and finally burns. It is soluble in 1,000 pts. of cold water, in 400 pts. of boiling water; in 265 pts. of alcohol of 90 per cent. at 10° , and in 33 pts. of boiling alcohol of the same strength; in 373 pts. of cold amyl alcohol, much more soluble in the same liquid warman; almost insoluble in aqueous ether; rather more soluble in alcohol than in ether; almost insoluble in benzene; soluble in 2,500 pts. of chloroform at 9° , and in 45 pts. at 56° . All the solvents dissolve morphin more readily and more copiously when it is freshly precipitated from solutions of its salts than when it has become crystalline.

Morphin combines with acids to form crystallizable salts, of which the hydrochlorid, sulfate and acetate are used in medicine. If morphin be heated for some hours with excess of HCl, under pressure, to 150° (302° F.), it loses water, and is converted into a new base, **apomorphin**, $C_{17}H_{17}NO_2$.

By heating together acetic anhydrid and morphin, **acetylmorphin**, $C_{17}H_{18}(C_2H_3O)NO_3$, and **diacetylmorphin**, $C_{17}H_{17}(C_2H_3O)_2NO_3$, are formed. The latter is used as a medicine under the name *heroin*. Similarly substituted **butyryl-**, **benzoyl-**, **succinyl-**, **camphoryl-**, **methyl-**, and **ethyl-morphin**, are also known. The last named is used medicinally under the name *dionin*.

Morphin is readily oxidized and is a strong reducing agent. It reduces the salts of gold and silver in the cold. It is oxidized by at-

mospheric oxygen when it is in alkaline solution, as well as by nitrous acid, potassium permanganate, potassium ferricyanid, or ammoniacal cupric sulfate, with the formation of a non-toxic compound which has received the names, **pseudomorphin**, **oxymorphin**, **oxydimorphin**, and **dehydromorphin** ($C_{17}N_{18}NO_3$)₂, whose molecule consists of two morphin molecules, united with loss of H_2 . **Morphin-sulfuric acid**, properly **morphylsulfuric acid**, or *monomorphyl sulfate*, $C_{18}H_{18}NO_2.O.SO_3H$, corresponds to ethyl sulfuric acid and phenyl sulfuric acid, and is obtained by the same method as the latter compound (p. 470) from morphin. It contains H_2O less than morphium sulfate, from which it differs in that the acidyl is attached through a hydroxyl, whereas in the salt it is attached to the nitrogen. When morphin is administered it appears in the urine as pseudomorphin, and also probably as morphylsulfuric acid, both of which are non-toxic. When morphin is distilled with powdered zinc, the principal product of the reaction is phenanthrene, accompanied by ammonia, trimethylamin, pyrrole, pyridin, and a product having the formula $C_{17}H_{11}N$, probably phenanthrene-quinolin.

The salts of morphium are crystalline. The *acetate* is a white crystalline powder, soluble in 12 parts of water, which decomposes on exposure to air, with loss of acetic acid. The *chlorid* is less soluble, but more permanent than the acetate. The *sulfate* is the form in which morphin is the most frequently used in medicine. It is a very light, crystalline, feathery powder; odorless, bitter, and neutral in reaction. It dissolves in 24 parts of water. Its solutions deposit morphin as a white precipitate on addition of an alkali. The crystals contain 5 Aq, which they lose at 130° (266 F.).

ANALYTICAL CHARACTERS.—(1) It is colored orange, changing to yellow, by HNO_3 . (2) A neutral solution of a morphium salt gives a blue color with neutral solution of ferric chlorid. (3) A solution of molybdic acid in H_2SO_4 (Fröhde's reagent) gives with morphin a violet color, changing to blue, dirty green, and faint pink. Water discharges the color. (4) Take two test-tubes. Into one (*a*) put the solution of morphin, into the other (*b*) an equal bulk of H_2O . Add to each a granule of iodic acid and agitate; *a* becomes yellow or brown, *b* remains colorless. To each add a small drop of chloroform and agitate: the $CHCl_3$ in *a* is colored violet, that in *b* remains colorless. Float some very dilute ammonium hydroxid solution on the surface of the liquid in *a*; a brown band is formed at the junction of the layers. (5) Moisten the solid material with HCl to which a small quantity of H_2SO_4 has been added, and heat in an air oven at 110° until HCl is expelled: a violet-colored liquid residue remains. Add to this a drop or two of water containing a little HCl , and neutralize with powdered sodium bicar-

bonate in slight excess: a pink or rose color is produced, most distinctly visible on the bubbles. Add a drop of water and a drop or two of alcoholic solution of iodine: a green color is developed. This reaction, known as the Pellagri test, is based upon the conversion of morphine into apomorphine, and consequently reacts with that alkaloid. (6) Moisten the solid with concentrated H_2SO_4 , and heat cautiously until white fumes begin to be given off, cool and touch the liquid with a glass rod moistened with dilute HNO_3 : a fine blue-violet color, changing to red and then to orange. If the H_2SO_4 contains oxides of nitrogen, as it usually does, a violet tinge will be produced before addition of HNO_3 , but then becomes much more intense. This reaction, known as the Husemann, may be applied by allowing the solid to remain in contact with H_2SO_4 for fifteen to eighteen hours in place of heating. (7) Marquis' reagent (3 cc. concentrated H_2SO_4 + 2 gtt. formalin) gives a brilliant red-violet color. These are the most important tests for morphine, and affirmative results with all of them prove the presence of that alkaloid. There are many others.

Codeine—Codeina (U. S.)— $\text{C}_{18}\text{H}_{21}\text{NO}_3$ + Aq—299 + 18—crystallizes in large rhombic prisms, or from ether, without Aq, in octahedra; bitter; soluble in 80 pts. cold water; 17 pts. boiling water; very soluble in alcohol, ether, chloroform, benzene; almost insoluble in petroleum-ether.

Codeine is the methyl ether of morphine, or its superior homologue, and resembles that alkaloid in some of its reactions; thus under similar circumstances both form apomorphine; and morphine may be converted into codeine by the action of methyl iodide in the presence of KHO. Codeine, however, only contains one OH group, and forms a monoacetyl derivative with acetyl chloride, while morphine produces a diacetyl compound.

Narceine— $\text{C}_{23}\text{H}_{27}\text{NO}_8$ + 2Aq—463 + 36—crystallizes in bitter, prismatic needles; sparingly soluble in water, alcohol, and amyl alcohol; insoluble in ether, benzene, and petroleum-ether.

Narcotine— $\text{C}_{22}\text{H}_{23}\text{NO}_7$ —413—crystallizes in transparent prisms, almost insoluble in water and in petroleum-ether; soluble in alcohol, ether, benzene, and chloroform. Its salts are mostly uncrystallizable, unstable, and readily soluble in water and in alcohol.

Narcotine is decomposed by H_2O at 140° (284° F.), by dilute H_2SO_4 , or by baryta, with formation of opianic acid, $\text{C}_{10}\text{H}_{10}\text{O}_5$, and hydrocotarnine, $\text{C}_{12}\text{H}_{15}\text{NO}_3$. Reducing agents decompose it into hydrocotarnine and meconine, $\text{C}_{10}\text{H}_{10}\text{O}_4$. Oxidizing agents convert it into opianic acid and cotarnine, $\text{C}_{12}\text{H}_{13}\text{NO}_3$.

Papaverine— $\text{C}_{20}\text{H}_{21}\text{NO}_4$ —crystallizes in prisms; almost insoluble in water, easily soluble in chloroform and in hot alcohol. It is optically inactive. It forms a colorless solution with concentrated

H_2SO_4 , which turns dark-violet when heated. Acetic anhydrid has no action upon it.

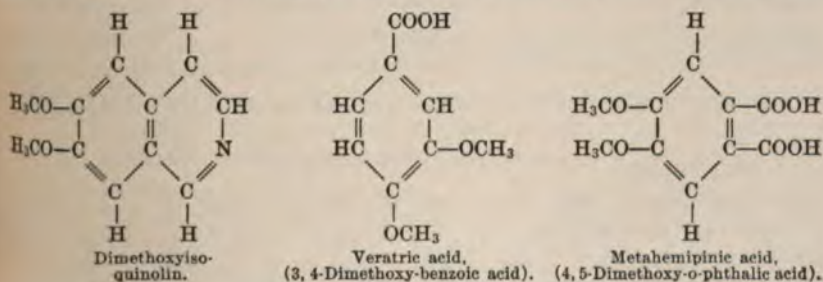
Thebain — Paramorphin — $\text{C}_{19}\text{H}_{21}\text{NO}_3$ —311—crystallizes in white plates; tasteless when pure; insoluble in water, soluble in alcohol, ether and benzene.

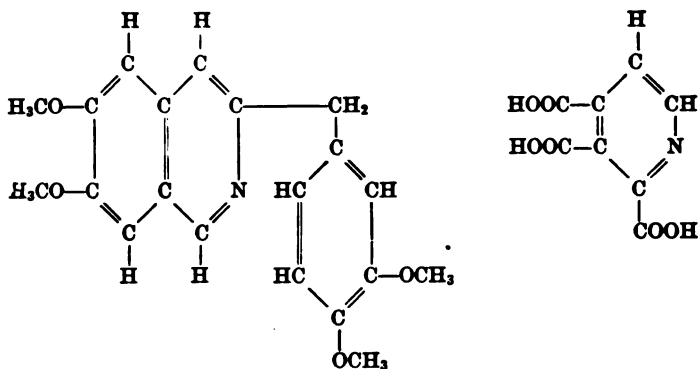
Apomorphin — $\text{C}_{17}\text{H}_{17}\text{NO}_2$ —is used hypodermically as an emetic in the shape of the chlorid. It is obtained by sealing morphin, with an excess of strong HCl , in a thick glass tube, and heating the whole to 140° (252°F.) for two to three hours. It is obtained also by the same process from codein. The free alkaloid is a white, amorphous solid, difficultly soluble in water. The chlorid forms colorless, shining crystals, which have a tendency to assume a greenish tint on exposure to light and air. It is odorless, bitter and neutral; soluble in 6.8 parts of cold water.

Relations and Constitution of the Opium Alkaloids.—The alkaloids of opium may be arranged in two groups: (I) Including those which are strong bases, are highly poisonous, and contain three or four atoms of oxygen; (II) those which are weak bases and contain four to nine oxygen atoms. So far as known, the alkaloids of the first group contain the phenanthrene-pyridin nucleus, while those of the second group are derivatives of isoquinolin. The six principal alkaloids above mentioned are equally divided between the two groups:

I.		II.	
Morphin	$\text{C}_{17}\text{H}_{19}\text{NO}_3$	Papaverin	$\text{C}_{20}\text{H}_{21}\text{NO}_4$
Codein	$\text{C}_{18}\text{H}_{21}\text{NO}_3$	Narcotin	$\text{C}_{22}\text{H}_{23}\text{NO}_7$
Thebain	$\text{C}_{19}\text{H}_{21}\text{NO}_3$	Narcein	$\text{C}_{23}\text{H}_{27}\text{NO}_8$

Papaverin was first recognized as an isoquinolin derivative. On oxidation of papaverin by potassium permanganate, **papaveraldin**, $\text{C}_{20}\text{H}_{19}\text{NO}_5$, is formed. This, on fusion with caustic potash, yields veratric acid, which is 3, 4-dimethoxy-benzoic acid, $\text{C}_6\text{H}_3.\text{COOH} : (\text{OCH}_3)_{2(3,4)}$, and dimethoxyisoquinolin, the constitution of the latter being established by its further decomposition into metahemipinic acid and α - β - γ -pyridin-tricarboxylic acid. The relations of papaverin and its products of decomposition are shown by the following formulæ:





Papaverin, (Tetramethoxy-benzyl-α-isoquinolin).

α-β-γ-Pyridin-tricarboxylic acid

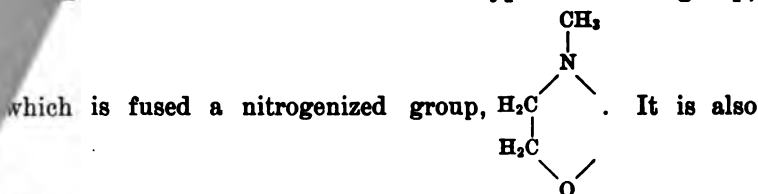
Narcotin, $C_{22}H_{23}NO_7$, is converted by oxidation into **opianic acid**, $C_{10}H_{10}O_5$ (p. 463), and **cotarnin**, $C_{12}H_{15}NO_4$. By hydrolysis it yields opianic acid and **hydrocotarnin**, $C_{12}H_{15}NO_3$; and by reduction, **meconin**, $C_{10}H_{10}O_4$ (p. 462), and **hydrocotarnin**. Narcotin, therefore, contains the nuclei of opianic acid, or of meconin, and of hydrocotarnin. The constitution of opianic acid is known, as well as that of its reduction product, meconin, but that of hydrocotarnin is not completely established. It is, however, a derivative of isoquinolin, containing one of the three methoxy groups (CH_3O) which exist in narcotin, and a bivalent group— $O.CH_2.O$ —attached to the benzene ring; and a methyl group, united to the N atom in the pyridin ring.

Narceïn, $C_{23}H_{27}NO_8$, is formed by the action of caustic potash upon narcotin iodomethylate: $C_{22}H_{23}NO_7.CH_3I + KHO = KI + C_{23}H_{27}NO_8$. Narceïn apparently does not contain an isoquinolin grouping, that which exists in narcotin having been broken in the above method of formation in such manner that the N is in a lateral chain in narceïn.

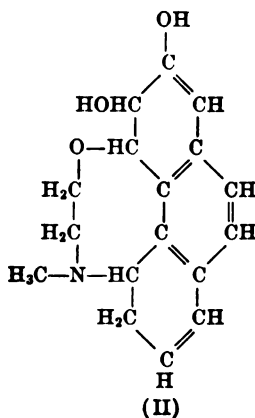
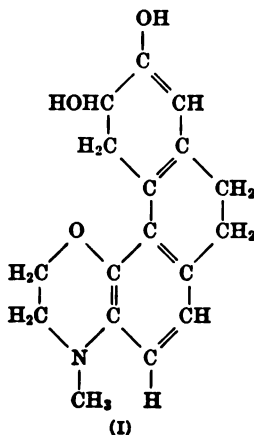
Morphin, $C_{17}H_{19}NO_3$, and **codeïn**, $C_{18}H_{21}NO_3$, are closely related. Codeïn is produced by the action of methyl iodid upon morphin-potassium: $C_{17}H_{18}KNO_3 + CH_3I = KI + C_{17}H_{18}(CH_3)NO_3$. It is, therefore, **methyl-morphin**. By the further action of methyl iodid upon codeïn in alcoholic solution, **codeïn methyl iodid**, $C_{18}H_{21}NO_3.CH_3I$, is produced, and this, when warmed with KHO, is converted into **methyl-morphin methine**, $C_{17}H_{19}NO_3:CH.CH_3$. The last-named substance is decomposed by acetic anhydrid into **methyldioxyphenanthrene** and **oxethyl-dimethyl-amin**: $C_{17}H_{19}NO_3:CH.CH_3 = C_{14}H_9 \begin{smallmatrix} \diagup OH \\ \diagdown O,CH_3 \end{smallmatrix}$

+ $N \begin{smallmatrix} \diagup CH_3 \\ -CH_3 \\ \diagdown CH_2.CH_2.OH \end{smallmatrix}$; and other morphin and codeïn derivatives are similarly decomposed, with formation, on the one hand, of a non-nitrogenized oxy-phenanthrene compound, and, on the other, an oxyamin or a trialkyl-amin. Upon these facts, it is concluded, that the

codein molecules consist of an oxyphenanthrene group,



recognized that the two hydroxyls are in the same phenanthrene ring, and that one of them is phenolic, the other alcoholic; also that one methyl group is attached to the nitrogen atom. The disposal of the hydrogen and hydroxyls in the phenanthrene nucleus and the position of attachment of the nitrogenized group above referred to remain undetermined. Two formulæ of constitution of morphin have been proposed, either of which is in consonance with the known facts:



The formula of codein is derived from either formula by substitution of CH_3 for H in the phenolic OH; that of apomorphin by removal of H_2O .

Thebain, $\text{C}_{19}\text{H}_{21}\text{NO}_3$, is decomposed by acetic anhydrid in a manner quite analogous to the decomposition of morphin, above referred to, but yielding a dimethoxy-phenolic derivative of phenanthrene, called thebaol, and methyl-oxethyl-amin: $\text{C}_{19}\text{H}_{21}\text{NO}_3 + \text{H}_2\text{O} = (\text{CH}_3\text{O})_2\text{C}_{14}\text{H}_7 \cdot$

$\text{OH} + \text{N} \begin{matrix} \text{H} \\ \diagup \\ \text{CH}_3 \\ \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \end{matrix}$. Like morphin and codein, it is therefore a phenanthrene-pyridin derivative.

Toxicology of Opium and its Derivatives.—Opium, its preparations and the alkaloids obtained from it are all active poisons. The alkaloids have not all the same action. In soporific effects, beginning with the most powerful, they rank thus: narcotin, morphin, codein; in tetanizing action: thebain, papaverin, narcotin, codein, morphin; in toxic action: thebain, codein, papaverin, narcein, morphin, narcotin.

The symptoms set in in from ten minutes to three hours, exceptionally "immediately," or only after eighteen hours. They are divisible into three periods: (1) a stage of excitement, marked by great physical activity, loquacity and imaginative power; is of short duration; longest in opium habitues, absent with large doses; (2) a period of sopor, in which there are diminished sensibility, weariness, contracted pupils, pale face, livid lips, drowsiness, increasing to deep sleep, from which, however, the patient may be roused, and when so roused is coherent in speech. This stage merges insensibly into the third, that of coma. The patient can no longer be aroused, even by violent means. The face is pale, the lips cyanosed, the muscular system completely relaxed, the reflexes abolished, the pupils contracted greatly, and insensible to light, the pulse slow, irregular, compressible, and finally imperceptible, the respiration more and more infrequent, stertorous, shallow, and accompanied by mucous râles. Retention of urine begins early in the poisoning. The usual duration of a fatal poisoning is from six to twenty-four hours. Deaths have occurred in forty-five minutes and in three days.

The minimum lethal dose for a non-habituated adult is probably 3 to 4 grains. Young children are very susceptible. Tolerance to a remarkable degree is established by habit, both in children and in adults, and instances are reported in which 50 to 60 grains have been taken daily, without toxic effects, by morphin-takers.

The treatment should consist in washing out the stomach with a dilute solution of potassium permanganate, leaving about 500cc. in the stomach, and in maintaining the respiration. In the first or second stage the "ambulatory treatment" should be adopted to prevent, if possible, the establishment of the third stage. If this stage develop, the main reliance is to be placed in maintaining the respiration by artificial methods, until the poison has been eliminated. Strong coffee, or caffèïn, by the mouth or rectum are of benefit. The same cannot be said of atropin. The urine should be drawn by the catheter.

The opiates leave no post-mortem lesions, except such as are usually observed after death from asphyxia, i. e., congestion of the vessels of the brain and meninges, and of the lungs, and a dark, fluid condition of the blood.

Alkaloids of unknown constitution.—Of the numerous alkaloids whose constitution is insufficiently known to permit of their classification, only a few can be here briefly considered:

Alkaloids of the Aconites.—The different species of *Aconitum* contain probably a number of alkaloids, but our knowledge of them is as yet extremely imperfect. The substances described as *aconitin*, *lycoctonin*, *napellin* are impure. It appears, however, that the principal alkaloids of *Aconitum napellus* and of *A. ferox*, although differ-

ing from each other, are both compounds formed by the union of aconin, $C_{26}H_{41}NO_{11}$, with the radical of benzoic acid in the former, and with that of veratric acid in the latter.

Aconitin — Acetylbenzoyl-aconin — $C_{26}H_{39}(CH_3.CO)(C_6H_5.CO)NO_{11}$ — the principal alkaloid of *A. napellus*, is a crystalline solid, almost insoluble in water, and very bitter. It is decomposed by H_2O at 140° (284° F.) and by KHO into aconin and acetic and benzoic acids. It is very poisonous.

Pseudo-aconitin — $C_{36}H_{49}NO_{12}$ — occurs in *A. ferox*. It is a crystalline solid, having a burning taste, and is extremely poisonous. On decomposition by H_2O at 140° (284° F.) it yields aconin and veratric acid.

Japaconitin — $C_{66}H_{88}N_2O_{21}$ — has been obtained from the root of *A. japonicum*, and is a crystalline solid which is decomposed by alkalies into benzoic acid and **japaconin**, $C_{26}H_{41}NO_{10}$.

The color reactions described as characteristic of "aconitine" are not due to the alkaloid.

TOXICOLOGY.—Aconite and "aconitine" have been the agents used in quite a number of homicidal poisonings.

The symptoms usually manifest themselves within a few minutes; sometimes are delayed for an hour. There is numbness and tingling, first of the mouth and fauces, later becoming general. There is a sense of dryness and of constriction in the throat. Persistent vomiting usually occurs, but is absent in some cases. There is diminished sensibility, with numbness, great muscular feebleness, giddiness, loss of speech, irregularity and failure of the heart's action. Death may result from shock if a large dose of the alkaloid be taken, but more usually it is by syncope.

The treatment should be directed to the removal of unabsorbed poison by the stomach-pump, and washing out of the stomach with infusion of tea holding powdered charcoal in suspension. Stimulants should be freely administered.

Alkaloids from other Sources.—**Ergotin** — $C_{50}H_{52}N_2O_3$ — and **Ecobolin** are two brown, amorphous, faintly bitter, and alkaline alkaloids obtained from ergot. They are readily soluble in water and form amorphous salts. The medicinal preparations known as ergotin are not the pure alkaloid.

Colchicin — $C_{17}H_{19}NO_5$ — occurs in all portions of *Colchicum autumnale* and other members of the same genus. It is a yellowish-white, gummy, amorphous substance, having a faintly aromatic odor and a persistently bitter taste. It is slowly but completely soluble in water, forming faintly acid solutions. It forms salts which are, however, very unstable.

Concentrated HNO_3 , or, preferably, a mixture of H_2SO_4 , and

NaNO_3 , colors colchicin blue-violet. If the solution be then diluted with H_2O , it becomes yellow, and on addition of NaHO solution, brick-red.

Veratrin—**Veratrina**, U. S.— $\text{C}_{32}\text{H}_{52}\text{N}_2\text{O}_8$ —occurs in *Veratrum officinalis* = *Asagracea officinalis*, accompanied by **Sabadillin**— $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_5$ —**Jervin**— $\text{C}_{30}\text{H}_{46}\text{N}_2\text{O}_3$ —and other alkaloids. The substance to which the name **Veratrina**, U. S., applies is not the pure alkaloid, but a mixture of those occurring in the plant.

Concentrated H_2SO_4 dissolves veratrin, forming a yellow solution, turning orange in a few moments, and then, in about half an hour, bright carmine-red. Concentrated HCl forms a colorless solution with veratrin, which turns dark-red when cautiously heated.

Physostigmin—**Eserin**— $\text{C}_{15}\text{H}_{21}\text{N}_3\text{O}_2$ —is an alkaloid existing in the Calabar bean, *Physostigma venenosum*. It is a colorless, amorphous solid, odorless and tasteless, alkaline and difficultly soluble in water. It neutralizes acids completely, with formation of tasteless salts. Its salicylate—**Physostigminæ salicylas**, U. S.—forms short, colorless, prismatic crystals, sparingly soluble in water.

Concentrated H_2SO_4 forms a yellow solution with physostigmin or its salts, which soon turns olive-green. Concentrated HNO_3 forms with it a yellow solution. If a solution of the alkaloid in H_2SO_4 be neutralized with NH_4HO , and the mixture warmed, it is gradually colored red, reddish-yellow, green, and blue.

Emetin— $\text{C}_{28}\text{H}_{40}\text{N}_2\text{O}_5$ —an alkaloid existing in *ipecacuanha* which crystallizes in colorless needles or tabular crystals, slightly bitter and acid; odorless, and sparingly soluble in water.

It dissolves in concentrated H_2SO_4 , forming a green solution, which gradually changes to yellow. With Fröhde's reagent it gives a red color, which soon changes to yellowish-green and then to green.

PTOMAINS, LEUCOMAINS AND TOXINS.

The name *ptomain*, derived from $\pi\tau\omega\mu\alpha$ ("that which has fallen," i.e., a corpse), was first suggested by Selmi in 1878 to apply to a substance, or class of substances, first distinctly recognized, although not isolated, by him, which are produced by saprophytic bacteria from proteins during putrefaction. The ptomains are sometimes referred to as "animal alkaloids," a term which is misleading, as they are produced from vegetable as well as from animal proteins, and but few of them are alkaloids in the present acceptation of the term (p. 545). The great majority, and those the best known, are monamins, diamins, guanidins, hydramins, betaïns, or amido acids. The term "ptomains" does not therefore apply to the members of a distinct class of chemical

compounds, but to the bacterial origin of substances belonging to several distinct chemical classes and also obtainable by other methods, having in common only the two qualities that they are basic and contain nitrogen. But some ptomaïns are true alkaloids. Some of the superior homologues of pyridin (p. 518) are putrid products. A base $C_8H_{11}N$, isomeric with collidin, formed during putrefaction of jelly-fish, on oxidation yields nicotinic acid, $C_5H_4N(COOH)$, which is also similarly produced from nicotin (p. 551), and also forms a chloroplatinate and an iodomethylate which have the characteristic properties of the like compounds produced from the pyridin bases (p. 517) and vegetable alkaloids. Other basic substances obtained from brown cod-liver oil, and probably formed by a modified putrefaction, are hydropyridin derivatives (p. 519). Among these are a dihydrolutidin, $C_7H_{11}N$, a dihydrocollidin, $C_8H_{13}N$, and a complex hydropyridic oxyacid, called morrhuic acid, $HO.C_5H_5N.C_3H_6.COOH$. Indole and skatole, products of putrefaction, also come within the definition of alkaloids.

Owing to the wide variations in the chemical constitution of the ptomaïns, they possess no characters by which they can be distinguished as a class. Some are strongly alkaline and basic, others only feebly so. Some are liquid, oily and volatile, others fixed and crystalline. Some are very prone to oxidation, and are active reducing agents, others are quite stable. For the same reason, no analytical method is possible by which vegetable alkaloids and ptomaïns can be separated from each other *en masse*, nor are any reactions known to which all ptomaïns respond while vegetable alkaloids do not, or the reverse; nor are such reactions to be expected. Certain classes of ptomaïns may be identified or separated from vegetable alkaloids, but not all. Thus those which are diamins may be separated by formation of their benzoyl derivatives (p. 385), but only a few ptomaïns are diamins. Those ptomaïns which are reducing agents give a blue color with a mixture of ferric chlorid and potassium ferricyanid but all ptomaïns do not reduce, and some vegetable alkaloids, such as morphin and veratrin, do. It was feared that the existence of ptomaïns, whose formation begins shortly after death, and also occurs during life, might render the detection of vegetable poisons in the cadaver impossible. Such fears were by no means groundless, as there is abundant evidence that ptomaïns have been mistaken for vegetable alkaloids in chemico-legal analyses. It is, however, possible to positively and certainly predicate the existence or non-existence in a cadaver of a given vegetable alkaloid, provided it have a sufficient number of characterizing reactions, but it can only be done after a thorough and conscientious examination by all physiological and chemical reactions.

The name *leucomaïn* is applied to basic nitrogenous substances,

such as the purin and pyrimidin bases, which are produced in living vertebrate organisms. But, as some leucomains, such as cholin, tyrosin, and betain, are also ptomaines, being produced by saprophytic bacteria, the line of distinction cannot be sharply drawn.

Toxins.—The name "toxin" was first used by Brieger, and by him applied to poisonous ptomaines and other toxic, basic, nitrogenous substances, obtained from the culture media of pathogenic bacteria or from animal organisms. Such are the four basic substances obtained from the culture media of the tetanus bacillus: **Tetanin**, $C_{13}H_{11}N_2O_4$, a yellow, strongly alkaline syrup; **Tetanotoxin**, $C_5H_{11}N$ (?), a volatile oil; **Spasмотoxin** and another unnamed base of undetermined composition, all of which form deliquescent hydrochlorids, and very soluble, crystalline platinochlorids. These bases, when injected into animals, cause clonic or tonic convulsions of great intensity, terminating in death. But it has been shown that the cultures from which these basic substances are obtainable, after filtration through porcelain, are vastly more toxic than the combined bases. These therefore can only constitute a small fraction of the active material produced by the bacilli, and the more virulent, non-basic product is a toxin in the more modern sense.

In this latter sense the toxins are poisonous substances of unknown chemical composition produced by bacteria or other cells. They are not products of decomposition of the proteins, as are the ptomaines, but synthetic products, secretions, as it were, of the bacteria. They are not all members of the same chemical class. Some, the **extracellular toxins**, so called because they pass in great part into the culture media, have many resemblances to the albumoses (p. 612). They are non-crystalline, soluble in water, and dialysable, are precipitated by alcohol and by ammonium sulfate, and lose their virulence when heated. The toxins of diphtheria and tetanus belong to this class. But little is known of the properties of the **intracellular toxins**, which are largely retained in the bacterial cells until these are destroyed, except that they do not dialyse, and are more resistant to heat than the extracellular toxins. The toxins of typhoid, tubercle and glanders belong to this second class.

The **toxalbumins** are substances obtained from certain seeds or secreted by animals, which are highly toxic, and have the general properties of albumoses or of globulins. They therefore differ from the toxins solely in that they are not of bacterial origin, and, furthermore, they resemble bacterial poisons more closely than vegetable alkaloids in their actions, particularly in the latent period preceding the manifestation of their effects.

The best studied of the vegetable toxalbumins is **ricin**, which exists in the castor-oil bean (*Ricinus communis*), being contained in

the press-cake, but not in the oil. It is extracted by 10 per cent NaCl solution, from which it is salted out by saturation with MgSO_4 . It is neutral in reaction, is precipitated by alcohol, gives the biuret reaction, and is destroyed by heat. Its lethal dose for rabbits is 0.04 mgm. per kilo. Other toxalbumins are: **abrin**, from jequirity (*Abrus precatorius*); **crotin**, from the seeds of *Croton tiglium*; **phallin**, from various toadstools (*Amanita*), and the toxic constituents of the venoms of serpents and of the poisonous secretions of spiders and insects.

PHYSIOLOGICAL CHEMISTRY.

The adjective "physiological" is here used in its proper sense. Physiology (*φυσιολόγος*=discoursing of nature) is defined as "the sum of scientific knowledge concerning the functions of living things." Chemistry has been defined as "that branch of science which treats of the composition of substances, their changes in composition, and the laws governing such changes." Therefore physiological chemistry has to do with the composition and changes in composition of living things, *whether they be in a normal or in an abnormal condition*. The medical tendency to distinguish between "physiological" and "pathological" chemistry, the former being considered as a branch of physiology, and the latter as a division of pathology, besides involving a solecism, is undesirable for four reasons: (1) The methods by which tissues and fluids are obtained from otherwise normal animal bodies for investigation are frequently such that they establish a pathological condition, and the extent to which the material so obtained is thus modified from the normal must always be taken into consideration in interpreting the results. (2) A solution of a doubtful question in normal physiological chemistry is frequently obtained by establishing a pathological condition, or by taking advantage of one occurring as a result of disease or accident, and comparing the composition of a tissue or fluid under these conditions with those from a normal subject. (3) Pathological chemical composition and processes are variations, either qualitative or quantitative, from the normal, and can therefore only be studied by comparison with the normal, hence the study of "physiological" and "pathological" chemistry must go hand in hand. (4) The substances most nearly concerned in the functions of life are of the most complex chemical constitution, and their study requires a high degree of chemical knowledge, patience and ingenuity. The physiological chemist must be a thoroughly trained chemist, equipped with sufficient medical knowledge for the study of this *chemical* specialty, not a physiologist or a pathologist who dabbles in chemistry.

Vegetable physiological chemistry is particularly of interest to the agriculturist, animal physiological chemistry to the veterinarian and the physician. Only the latter branch will be here considered.

The subject may be divided into two sections: (1) the study of the properties, physical and chemical, of the various substances (proximate principles) which occur in living bodies; (2) that of the chemical changes, chemical processes, which take place in living organisms, which obviously involves the consideration of the composi-

tion, and the variations therein in health and disease of animal tissues and fluids. The first division is a part of pure chemistry, and has been considered in the preceding pages, except in so far as it relates to the albuminous substances, or proteins, which being still of undetermined constitution find no certain place in the classification of organic compounds, and, on the other hand, being intimately associated with the chemical processes of life, may be suitably considered here.

PROTEINS.

Representatives of this class of substances are never absent from living animal or vegetable cells, to whose "life" they are indispensable. They are for the most part uncrystallizable, although the hæmoglobins crystallize readily, as do certain vegetable proteins, and the true albumins may be obtained in crystals. Some are soluble in pure water, others only in the presence of other substances, and others are insoluble in water. They are insoluble in alcohol, ether, chloroform or benzene. With the exceptions of the peptones and some albumoses, they dialyse only very slightly, or not at all; they are typical "colloids" (p. 18). They retain foreign substances, such as coloring matters, mineral salts, etc., with great tenacity, whether in their solutions or when separated therefrom, and have not, therefore, been obtained "ash-free." They are lævogyrous, except the nucleoproteids, which are dextrogyrous. They are composed of carbon, hydrogen, oxygen and nitrogen. Most of them also contain sulfur, and some contain phosphorus; others, iron, copper, or iodine. Their molecular weights are very large, probably greater than 10,000. Their constitution is unknown, and no substance has as yet been obtained synthetically which is identical with a natural protein, although substances have been thus produced having many of the properties of gelatins or albumoses. The native albumins are neutral and non-ionized in their solutions, but they may become ionized, and behave both as bases and acids, in the presence of other ions.

Coagulation.—All native albumins are separated as solids or semisolids when their very faintly acid solutions, containing minute quantities of salts, are heated. This separation is called **coagulation**, and the coagulated albumin is said to be **denaturized**, because it has been so changed that it cannot be again brought into its original form of solution. Certain proteins, such as the histons (p. 587), may be coagulated by heat without being denaturized, i.e., they may be redissolved in their own form. Albumins may also be denaturized without being coagulated. This occurs when heat is applied to their alkaline or strongly acid solutions; when alkali- or acid-albuminates are formed, which, although denaturized from the parent albumin, remain in solu-

tion. With faintly acid reaction the coagulation is complete. The temperature at which coagulation takes place varies with different albumins, but is fairly constant for each individual protein, and is referred to as its **coagulation temperature**, which is one of the factors for its identification. The coagulation temperature is, however, affected by the amount of salts present, the most favorable concentration being about 1 per cent of sodium chlorid, and to a greater extent by the presence of certain nitrogenous compounds, such as cholin, pyridin, anilin and urea. Solid albumins, unaltered and soluble in their original form, may be obtained by evaporation of their solutions at temperatures below their coagulation temperatures.

Denaturization and coagulation are also caused by agencies other than heat: by long agitation or even prolonged standing of solutions of the albumins; by agitation of such solutions with ether or chloroform; by the mineral acids, particularly nitric acid; by certain metallic salts, such as HgCl_2 , $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$, CuSO_4 , Fe_2Cl_6 , or $\text{K}_4\text{Fe}(\text{CN})_6$, the last in the presence of acetic acid; by "alkaloid reagents," such as tannin, phosphotungstic and phosphomolybdic acids, tungstates, potassium iod-hydrargyrate, or iodobismuthate in acid solution; by chloral, picric acid, salicylsulfonic acid, trichloroacetic acid, and phenol. Formic aldehyde produces denaturization without coagulation if the reaction be acid or alkaline.

Certain native albumins, such as fibrinogen, myosin, and gluten-casein, are also converted into denaturized products, not returnable to the original form, by contact with porous substances, or by the action of enzymes.

Precipitation.—When alcohol is added to an albuminous solution the albumin is precipitated, without immediately suffering other change, and may be redissolved in its primitive form. But by prolonged contact with alcohol it suffers denaturization and coagulation.

Native albumins and albumoses are precipitated unchanged from their solutions by the addition thereto of certain neutral salts, either in the solid form or in saturated solution. This method of precipitation (which is also resorted to in the soap industry) is known as **salting out**. Ammonium sulfate and zinc sulfate are the most efficient agents for this purpose, and precipitate all native albumins and albumoses completely, while sodium chlorid, sodium sulfate, magnesium sulfate, etc., precipitate only certain classes of proteins. The quantity of a given salt, i. e., the concentration of the salt solution, which is required to precipitate the several proteins is quite constant for each species, but varies with different species. The more complex the protein (and therefore the greater its molecular weight), the more readily it is **salted out**. Thus fibrinogen may be completely precipitated by half saturation in neutral solution with the less active sodium chlorid, while a

deuteroalbumose requires complete saturation with the more active ammonium sulfate in acid solution for complete precipitation. An acid reaction favors salting out to such an extent that the differentiations referred to below are only observed in neutral solutions. Each species of albumin or albumose requires the addition of a certain proportion of salt to its solution before precipitation begins, and for each there is definite concentration at which precipitation is complete, and beyond which, of course, increase of concentration produces no effect. These **upper and lower limits** are constant for any given species, the lower somewhat less so than the upper, and are utilized for the identification and separation of the several species. For the determination of these limits varying graduated quantities of a neutral, cold saturated solution of the salt are added to samples of fixed volume (2 cc.) of the protein, the mixtures diluted to fixed volume (10 cc.), agitated, and allowed to stand for a half hour. The lower limit is between the concentration of the most dilute sample in which turbidity is produced and the one next below which remains clear. The turbid samples are then filtered, and the filtrates treated with a small additional quantity (0.1 cc.) of the salt solution. The upper limit is between the concentration of the most concentrated filtrate in which this addition causes turbidity, and that next above which remains clear. Both limits are more closely determined by further experiment within the limits thus ascertained. Thus the upper and lower limits of fibrinogen with ammonium sulfate are 1.6 and 2.6 respectively, and those of serum albumin are 6.4 and 9.0, which means that in a solution of serum albumin, water and saturated salt solution, in 10 cc. of which there are contained 6.4 cc. of saturated salt solution, precipitation begins; and in one containing 9 cc. of saturated salt solution in 10 cc. precipitation is complete. The limits are also expressed in percentages of saturated salt solution; thus 64 per cent and 90 per cent for serum albumin.

Although the proteins precipitated by salting out are not denatured, and may be redissolved unchanged from their primitive form, they tenaciously retain a portion of the salt, which cannot be separated by dialysis; and in some cases they retain the anion in a form of combination from which the acid cannot be removed by water. Thus serum albumin forms a sulfate with the anion of ammonium sulfate.

Color Reactions.—The color reactions of the proteins are not peculiar to them, but depend upon the existence in them of certain chromic groupings which also occur in other substances. While, therefore, they do not serve for the identification of the proteins unless taken collectively, they are of notable interest as indicating the existence in those protein molecules which respond to a given reaction, of that grouping which that reaction characterizes.

Xanthoproteic Reaction.—If a solid protein be moistened with concentrated HNO_3 , a yellow color is produced which, on addition of NH_4HO , changes to orange, or, on addition of NaHO , to reddish-brown. With solutions of native albumins a white coagulum is produced in the cold, which later becomes yellow. This reaction depends upon the presence of the tyrosin grouping, or that of indole.

Millon's Reaction.—A purple-red color when a solid protein is warmed with Millon's reagent to about 70° . With solutions of proteins a white coagulum is formed in the cold, which assumes the red color when warmed. The reagent is made by dissolving, by the aid of heat, 1 pt. of Hg in 3 pts. of HNO_3 , sp.gr.1.42, diluting with 2 vols. H_2O , and decanting after 24 hours. It contains mercurous and mercuric nitrates and some nitrous acid. This reaction is usually ascribed to the presence of a single phenolic hydroxyl. But the color given by phenol, cresol, salicylic acid, etc., is a red-orange, rather than the purple-red of the proteins, and the two naphthols give a yellow color, without any tinge of red. It is also said that the introduction of a second OH changes the color to yellow, but the color with hydroquinone is not to be distinguished from that with phenol. Tyrosin, which contains both phenol and amido groups, reacts frankly with Millon's reagent, and the similar reaction of the proteins is probably due to presence in them of the tyrosin grouping.

The Biuret Reaction.—A violet or red color with an excess of KHO or NaHO and a few drops of a 2 per cent solution of CuSO_4 and heat. With the native albumins the color is blue-violet or red-violet, and with the albumoses, peptones and higher polypeptids distinctly red. The reaction is given by compounds containing two CO.NH_2 groups, or one such group and one CH_2NH_2 group (p. 407), and seems to depend upon the existence of the polypeptid groups (p. 415) in the protein molecule. This is the only one of the color reactions to which the simplest of the proteins respond.

Adamkiewicz Reaction.—If glyoxylic acid (obtained in solution by reducing a solution of oxalic acid by sodium amalgam) be added to a solution of a protein, the solution floated upon the surface of concentrated H_2SO_4 , and the mixture heated, a ring of color is produced at the junction of the layers, red, green, then violet, and the whole liquid becomes violet when the layers are mixed. The reaction depends upon the presence of the tryptophane group (p. 540), and is not given by gelatin.

Liebermann's Reaction.—The protein, freed from fat by extraction with ether and hot alcohol, is dissolved by boiling in concentrated HCl to which a drop of concentrated H_2SO_4 has been added, forming a deep violet-blue solution. This is probably also a tryptophane reaction.

Molish's Reaction (p. 323) is given by proteins containing a carbohydrate group.

Decompositions.—The study of the decomposition products of the proteins by oxidizing agents, by fusion with mineral alkalies, by boiling with dilute acids or alkalies, by the action of proteolytic enzymes, by those of other hydrolysing agencies, and by other means, is of great interest, being the means by which knowledge of the constitution of these complex molecules must be sought for. By the action of the less energetic of these decomposing agents compounds are obtained which are of more complex structure than those produced by more active agencies, although the simpler products of decomposition may also accompany those of higher molecular weight, as by-products of less complete decompositions. The more complex products represent in their "radicals" certain "groupings," or "atomic complexes," which, we have every reason to believe, constitute integral parts of the protein molecular structure, as the esters are constituted of the "atomic complexes" of the acid and alcohol.

Active oxidizing agents attack the protein molecule profoundly, yielding products which are for the most part far removed from the original substance, and which are themselves products of decomposition of the "atomic complexes" above referred to; acids and aldehydes of the fatty, oxalic and benzoic series and their nitrils, including hydrocyanic acid, ketones, amido acids, carbon dioxid, and ammonia. With HNO_3 various nitro derivatives are obtained, and with Cl, Br and I halid derivatives. By oxidation with $\text{K}_2\text{Mn}_2\text{O}_8$ an acid, **oxyproto-sulfonic**, containing the sulfonic group, is formed, and by continued oxidation **peroxyprotonic acid**. In oxidation with BaMn_2O_8 guanidin is one of the products.

Fusion with caustic alkalies also causes deep decomposition, the products being ammonia, mercaptan, fatty acids, amido fatty acids, tyrosin, indole and skatole.

By boiling with dilute mineral acids, or with $\text{HCl} + \text{SnCl}_2$, the proteins are hydrolysed with formation of hydrogen sulfid, ethyl sulfid and ammonia as simple products, and amido acids, hexon bases (p. 417), pyrrolidin and oxypyrollidin carboxylic acids (p. 511), and **melanoidins**, the last named being also products of decomposition of the **melanins**, substances to which the hair and other dark portions of the body owe their color. The amido acids, including serin, tyrosin and cystin, produced in this and other hydrolytic decompositions probably exist in the proteins as polypeptids, formed by the union of several amido acid complexes (p. 415).

Considering the nitrogen which is split off, in more or less complex combination, on hydrolysis of proteins by boiling with dilute acids, it appears to have existed in the parent protein in five forms of combi-

nation, corresponding to five classes of decomposition products: (1) Easily separable, so-called amino-nitrogen, given off as NH_3 ; (2) Urea forming nitrogen, in the guanidin remainder of arginin (p. 418); (3) Basic nitrogen, or diamido nitrogen, contained in basic nitrogen compounds, precipitable by phosphotungstic acid; (4) Monamido nitrogen, in monamido acids; (5) Humus nitrogen, in humus-like melanoidins, dark-colored, amorphous, nitrogenous remainders.

The quantitative distribution of nitrogen in these five groups differs in different proteins: (1) is entirely absent in protamins; 1-2 per cent in gelatin; 5-10 per cent in other animal proteins; 13-20 per cent in vegetable proteins. (2) In protamins 22-44 per cent; in histons 12-13 per cent; in gelatin 8 per cent; in other proteins 2-5 per cent. (3) In protamins 63-88 per cent; in histons 35-42 per cent; in other animal proteins 15-25 per cent; in vegetable proteins 5-37 per cent. (4) The greater part of the nitrogen, 55-76 per cent, in proteins other than protamins is in this form. (5) Varies within wide limits.

The sulfur, the amount of which varies greatly in different proteins, is given off on hydrolysis as cystin, cystein, α -thiolaetic acid, mercaptans and ethyl sulfid.

The nitrogen-containing products of hydrolysis of proteins may be thus classified:

I. Aliphatic. A. Containing no sulfur:

(1) Guanidin remainder. $\text{H}_2\text{N}:\text{C}:\text{NH}'$ (+ornithin=arginin);

(2) Monobasic monamido acids: glycocoll, alanin, amido-valerianic acid, leucin, serin;

(3) Dibasic monamido acids: aspartic and glutamic;

(4) Monobasic diamido acids: ornithin, lysin;

B. Containing nitrogen and sulfur: Cystin, cystein;

II. Carbocyclic: phenylamidopropionic acid, tyrosin;

III. Heterocyclic: A. Pyrrole derivatives: pyrrolidin and oxyrrolidin carboxylic acids;

B. Glyoxalin derivatives (?): histidin;

C. Indole derivatives: indole, skatole, tryptophane.

All proteins except the protamins and some of the peptones contain sulfur. One fraction of this, referred to as "loosely combined" sulfur is given off as hydrogen sulfid by boiling with alkaline solutions. It is this fraction which causes the formation of a brown or black color or even a black precipitate, when a protein is heated with a solution of caustic alkali in presence of lead acetate, in the "sulfur test" for the proteins. The second fraction is not separable in this manner, but only, as a sulfate, by fusion with saltpetre and sodium carbonate, or, as a sulfid, by fusion with caustic potash. The ratio of loosely combined sulfur to total sulfur varies notably in different proteins.

from $\frac{2}{3}$ in serum albumin to $\frac{1}{2}$ in hæmoglobin. It would appear from this constant difference in separability of different portions of sulfur from proteins that the molecules of these substances must contain at least two atoms of sulfur in different forms of combination. This conclusion, is, however, invalidated by the fact that both cystin and cystein only give off one-half of their sulfur, and that very slowly, by boiling with alkaline solutions, yet the two atoms of sulfur in cystin are symmetrically combined, and the molecule of cystein contains but one sulfur atom.

Many proteins, not only the glycoproteids (p. 594), but also true albumins, as egg albumin, serum albumin, serum globulin, the nucleoproteids, etc., react with Molisch's reagent (p. 323), and, on hydrolysis, split off a carbohydrate group, which is an amido-sugar, usually glucosamin, $\text{CHO} \cdot \text{CHNH}_2 \cdot (\text{CHOH})_3 \cdot \text{CH}_2\text{OH}$ (p. 387), probably existing in the protein as a polysaccharid complex. Some of the nucleoproteids yield a pentose group, others lævulinic acid. Other proteins, as casein, myosin, and fibrinogen yield no carbohydrate.

The decomposition of proteins by the proteolytic enzymes, pepsin, trypsin and papaïn, consists of a series of hydrolyses and results, first in the formation of albumoses and peptones, and later, by trypsin particularly, of polypeptids, amido acids, hexon bases, tryptophane, amins, diamins and ammonia. These changes occur in the processes of digestion, and will be discussed later.

Putrefaction is the decomposition of dead protein material under the influence of certain bacteria, attended by the evolution of more or less fetid products. In order that it may occur, certain conditions are necessary: (1) The presence of living bacteria, or of their germs; (2) the presence of moisture; (3) a temperature between 5° and 90° ; (4) an atmospheric condition suitable to the growth of the bacteria. Some of the several species of bacteria which cause putrefaction are aerobic, i. e., they require the presence of air for their development, while others are anærobic, i. e., they thrive best in the absence of oxygen. The first products of putrefaction are the same as those produced by proteolytic enzymes: albumoses and peptones. The later products vary with the conditions under which putrefaction occurs. The most prominent are: (1) Inorganic products such as N, H, H_2S , NH_3 , and simple organic compounds such as CO_2 and hydrocarbons; (2) acids of the fatty, oxalic and lactic series; (3) amido acids, such as α -amidovalerianic acid and leucin; (4) aliphatic monamins, as trimethylamin; diamins, as putrescin, from arginin, and cadaverin, from lysin; and hydramins, as cholin, muscarin and neurin; (5) aromatic products, among which are: (a) tyrosin and its derived products, phenol, cresol, p-oxyphenylacetic acid, and p-oxyphenylpropionic acid; (b) indole, skatole, skatole-carboxylic acid, and skatoleacetic

acid, derived from the tryptophane complex; (c) phenylamidopropionic acid and its derivatives, phenylethylamin, phenylacetic acid, and phenylpropionic acid; (d) ptomains of undetermined constitution, belonging to the aromatic series; pyridin derivatives. Under certain imperfectly defined conditions buried protein material does not undergo ordinary putrefaction, but is converted into a substance resembling tallow, and called *adipocere*, which consists chiefly of ammonium palmitate, stearate and oleate, calcium phosphate and carbonate, and an undetermined nitrogenous substance.

Classification of Proteins.—A chemical classification of proteins, based upon their constitution, is at present manifestly impossible, and any other classification can be only tentative, and probably temporary. For a provisional classification some of the proteins arrange themselves naturally in fairly well-defined groups, according to their products of decomposition and their solubilities, while others, of quite diverse characters, must be still arranged in the miscellaneous group of the "albuminoids." Probably the Hammarsten-Cohnheim classification is the most satisfactory for the present:

A. True, or Native Albumins:

a. Albumins—soluble in pure water; coagulated by heat. Serum albumin, ovalbumin, lactalbumin.

b. Globulins—insoluble in pure water, soluble in dilute solutions of neutral salts; coagulated by heat. Serum globulins, oviglobulins, lactoglobulin, cell globulins, vegetable globulins.

c. Coagulating Albumins—yielding coagulated products by the action of enzymes. Fibrinogen, myogen, myosin, glutenprotein.

d. Nucleoalbumins—almost insoluble in pure water, or in solutions of neutral salts, easily soluble in slight excess of alkalies; contain phosphorus; on peptic digestion yield pseudonucleins. Casein, vitellins, phytovitellins, mucin-like nucleoalbumins.

e. Histons—contain 35–42 per cent of their nitrogen as basic nitrogen.

d. Protamins—contain 63–88 per cent of their nitrogen as basic nitrogen.

The histons and protamins do not exist as such in nature, but are most conveniently classified in this group.

B. Derived Albumins:

a. Albuminates—insoluble in water or in salt solution, except in presence of acid or alkali; derived from native albumins by the action of acids or alkalies. Acid-albuminates, alkali-albuminates.

b. Albumoses—Propeptones—soluble in dilute salt solutions, precipitated by cold HNO_3 , redissolved on heating.

c. Peptones—very soluble in water, readily dialysable, give none of the protein reactions except the biuret reaction.

d. Coagulated albumins—insoluble in water and in salt solutions; obtained from native albumins by the action of heat, of strong mineral acids, or of enzymes, and do not regenerate the parent protein. Coagulated albumins and globulins and fibrin.

C. Proteids.

a. Hæmoglobins—decomposable into an albumin and a crystalline pigment or chromogen.

b. Nucleoproteids—yield nucleic acids and native albumins on decomposition. Nucleohiston, etc.

c. Glycoproteids—decomposable into a reducing substance and a native albumin. Mucin, mucoids, phosphoglycoproteids.

D. Albuminoids—proteins not included in one of the above classes. Keratins, collagen, elastin, spongin, fibroïn, amyloid, albumoid, reticulin, ichthylepidin, etc.

NATIVE ALBUMINS.

Albumins—are soluble in water, in dilute salt solutions, and in dilute acids and alkalies. They are coagulated by heat, by excess of mineral acids, and by certain metallic salts. They are salted out by NaCl and MgSO_4 only in acid solution, but are precipitated by $(\text{NH}_4)_2\text{SO}_4$ in neutral solution, in which the limits are 6.4 and 9.0 (p. 577). They are capable of crystallization. On hydrolysis they yield 6.34–8.53 per cent of their nitrogen as ammonia, 67.8 per cent as monamido nitrogen, and 21.3 per cent as diamido nitrogen. They yield 1.5–2.0 per cent of tyrosin, and 0.29–2.53 per cent of cystin, and contain a larger proportion of sulfur, 1.6–2.2 per cent, than other proteins except the keratins. (See Serum albumin under Blood, Urine; Lactalbumin, under Milk, and Ovalbumin (p. 584).

Globulins—are insoluble in pure water; soluble in dilute salt solutions, and in very dilute acids or alkalies. They are precipitated from these solutions by dilution with a large quantity of water, by dialysis (See Serum globulin, p. 652), by dilute mineral acids and by acetic acid, or by CO_2 . An excess of CO_2 , however, redissolves the precipitate. They are completely salted out by saturation with MgSO_4 ; only partly by saturation with NaCl. Their limits with $(\text{NH}_4)_2\text{SO}_4$ are 2.9 and 4.6. The precipitates obtained by salting, soluble at first, become coagulated and insoluble on standing. They are coagulated by heat. They have not been crystallized. On hydrolysis they yield 8.9 per cent of their nitrogen as ammonia, 68.3 per cent as monamido nitrogen, and 24.9 per cent as diamido nitrogen. They yield 3 per

cent of tyrosin, and 1.5 per cent of cystin, and contain less sulfur than do the albumins, 0.97 per cent (See Blood, Urine, Milk).

White of Egg.—The "white" or "albumen" of hens' eggs consists of a yellowish fluid, enclosed in a delicate network of connective tissue (keratin). The fluid portion, separated by beating and filtration through muslin, is alkaline, sp.gr. 1.045, and coagulates to a dense, opaque, white mass when heated. But if the eggs have been soaked in a solution of caustic alkali for three days, the "white" remains transparent when heated. This is due to the formation of an alkali-albumin, which is also obtained without alkaline treatment from the eggs of nesting birds, and is called "tata-albumen." Egg albumen contains 800–880 p/m of water, and 120–200 of solids, which latter contain 100–130 proteins, 3–7 salts, and traces of fat, lecithins, cholesterol, and a carbohydrate. The proteins of white of egg are at least five in number: 67 per cent of the 100–130 above referred to consist of two **oviglobulins**, coagulated at 57.5° and 67° , partly precipitable by dilution with water, and completely by salting with MgSO_4 . There are three **ovialbumins**, differing in coagulation temperatures: 67° , 72° , and 82° ; and in specific rotary power: $[\alpha]_D = -25.8^{\circ}$, -34.2° , and -42.5° , all of which are lower than the value of $[\alpha]_D$ for serum albumin, -62.6° to -64.6° . These ovialbumins also differ from serum albumin in that they appear in the urine when injected into the circulation, which serum albumin does not do in health. Ovialbumin may be caused to crystallize in needles by removal of globulins from perfectly fresh egg albumen by partial salting with $(\text{NH}_4)_2\text{SO}_4$, slow evaporation of the solution at the ordinary temperature, and recrystallization. The carbohydrate above referred to appears to exist in the form of a glycoprotein, containing 15 per cent of carbohydrate, and 1.18 per cent of sulfur. **Ovomucoid** is a pseudopeptone, constituting about 10 per cent of the proteins of white of egg. It is not precipitated by mineral acids, except phosphotungstic acid, and is obtained, after removal of the albumins and globulins by heat and acetic acid, by precipitation with alcohol.

The classes of **vegetable albumins** and **vegetable globulins** are not sharply differentiated, as the latter are not entirely insoluble in pure water. Both are coagulated by heat. The effect of NaCl upon solutions of vegetable globulins also varies with the proportion of salt added; a small amount causing a precipitate, which redissolves in larger proportion, and is again precipitated by a further addition of salt. Wheat flour contains 0.26 to 0.30 per cent of protein coagulable by heat, and 1.55 to 1.90 per cent of protein material not so coagulable. **Conglutin**, a protein obtained from the lupines and from almonds, has most nearly the character of the globulins, being soluble in salt solutions of 5 to 10 per cent, and precipitable therefrom by

dilution with water. A similar globulin accompanies legumin in peas.

Coagulating Albumins—exist in nature in solution, and change to a coagulated product "spontaneously," i. e., by a process the nature of which is imperfectly understood, but which is usually attributed to enzyme action. Certainly coagulation of these substances occurs by a different process from that which brings about the coagulation of albumins and globulins by heat, mineral acids, etc.

The most important member of this group is fibrinogen, the precursor of fibrin, which will be considered under "Blood" (p. 651).

When muscular tissue, freed from blood, and immediately after death, is expressed, a liquid is obtained which is called the **muscle-plasma**, and the remaining solid is the **muscle-stroma**. The liquid, on standing, separates into a coagulum of **myogen-fibrin** and **myosin-fibrin**, and a liquid, the **muscle-serum**. While the muscle-plasma is neutral or faintly alkaline, the muscle-serum is acid in reaction. Myogen-fibrin is formed by coagulation of a protein, **myogen**, existing in solution in the plasma. The formation of muscle-fibrin is comparable with the formation of fibrin from fibrinogen in coagulation of the blood, and, corresponding to the fibrinoglobulin produced from fibrinogen, but in larger amount, a portion of the myogen fibrin remains in the serum as **soluble myogen-fibrin**.

Myogen is obtained from muscle-plasma, after removal of myosin (below) by addition of $(\text{NH}_4)_2\text{SO}_4$ to 28 per cent and filtration, by further addition of $(\text{NH}_4)_2\text{SO}_4$ to near saturation. The precipitated soluble myogen-fibrin is then removed, after washing with saturated $(\text{NH}_4)_2\text{SO}_4$ solution, by resolution in water, and coagulation at 40° and filtration.

Myogen is soluble in water, from which it is completely precipitated by saturation with $(\text{NH}_4)_2\text{SO}_4$, and partly by NaCl or MgSO_4 . It is only partly precipitated by alcohol, and not by dialysis. Acetic acid and mineral acids convert it into acid-albuminate, and it is only precipitated by CO_2 in presence of neutral salts. It is therefore more closely allied to the albumins than to the globulins. It coagulates about 60° . Soluble myogen-fibrin is precipitated by dialysis, coagulates at 40° , and is gradually converted into the insoluble form in presence of neutral salts. Myogen constitutes about 80 per cent of the proteids of muscle-plasma.

Myosin, the second protein of muscle-plasma, constitutes the remaining 20 per cent of its total proteins, and is precipitated by partial saturation with $(\text{NH}_4)_2\text{SO}_4$ to 28 per cent. It is not soluble in pure water, but soluble in dilute salt solutions, from which it is precipitated by dilution with water, by dialysis, and by CO_2 , in which respects it resembles the globulins. It is almost completely precip-

itated by alcohol, and by dilute acids or alkalis. Greater quantities of acid or alkali convert it into albuminates. It begins to coagulate at 35° and does so completely at 50° . When coagulated it constitutes **myosin-fibrin**. Whether or no the formation of muscle fibrins has a causative relation to the phenomenon of post-mortem rigidity is uncertain. Myosin-like proteins, having the same coagulation temperature as muscle myosin, have also been obtained from other tissues, spleen, thymus, leucocytes, etc.

Gluten-protein is a precursor of gluten, existing in wheat and other grains, which has the characters of a globulin, and is supposed to form gluten by enzyme action.

Nucleoalbumins, also called **phosphoglobulins**, from their phosphorus content and their resemblance to the globulins, include casein (see Milk, p. 763), ovivitellin, ichthulin and phytovitellins. They contain phosphorus, 0.43 per cent in ichthulin, 0.85 per cent in casein, and 5.19 per cent in ovivitellin, and also traces of iron. They behave as acids, are almost insoluble in water, soluble in very weak alkaline solutions, very sparingly soluble in dilute salt solutions, and are not coagulated by heat. On peptic digestion they yield **para-** or **pseudo-nucleins** as amorphous, sparingly soluble residues, which contain the major part, if not the whole of the phosphorus. They resemble the nucleoproteids and the glycoproteids, but differ from the former in that they yield no xanthin bases on decomposition, and from the latter in that they yield no reducing substance under like conditions.

The **yolk** of hens' eggs contains 572-515 p/m of water, and 485-428 p/m of solids. The latter consist of 213-228 p/m of fats, 156-158 of proteins, 84-107 of lecithins, 4-17 of cholesterin, and 33 of salts, besides cerebrin and a coloring matter, a lutein. In the ash the K salts exceed the Na salts; the Ca salts are present in notably large amount, 12-13 per cent of the ash; and the amount of phosphoric acid is also large, 64-67 per cent. The principal protein is **ovivitellin**, a nucleoalbumin, whose pseudonuclein is **avivitellinic acid**, which contains 9.88 per cent of phosphorus and 0.57 per cent of iron in organic combination; yields small quantities of arginin and histidin on decomposition, and gives the Millon and biuret reactions. Ovivitellin has not been obtained free from lecithins, which may indicate that the two substances exist in chemical combination, as a **lecithalbumin**, although this is uncertain.

The eggs of fish (carp) contain a nucleoalbumin, called **ichthulin**, which on decomposition by alkalis yields a pseudonuclein, **ichthulinic acid**, which contains 10.34 per cent of phosphorus, but no iron. In a crystalline form it constitutes the **yolk-platelets**.

The **phytovitellins**, or **phytoglobulins**, occurring in the vegetable world, are related both to the globulins and to the caseins. They are

acid in character, being precipitated by acids, although soluble in excess; and soluble in dilute alkalies, from which solutions they are precipitated by dilution with water, and by dialysis. In dilute solution they coagulate at 75° , but in concentrated solution only in part, or at a more elevated temperature. In dilute solution they are coagulated by HNO_3 , but the coagulum redissolves in excess or on heating. They give the protein color-reactions, including a red color with the biuret reaction. They form crystals quite readily. That from Para nuts crystallizes in octahedra, containing Ca and Mg, and is one of the constituents of the **aleurone corpuscles**, which are granules having the appearance of those of starch, but giving a brown color with iodine, which occur in Para and other nuts. **Legumin** occurs in peas, beans, etc. It contains 0.35 per cent of phosphorus; on peptic digestion it yields a pseudonuclein containing 1.83 per cent of phosphorus; and it forms a solution in water which gelatinizes when heated. **Edestin** is a crystalline phytovitellin obtained from various seeds, notably those of hemp. **Gluten** is a protein material existing in wheat, which remains insoluble and forms a soft, but tough, elastic paste when the flour is kneaded in a stream of water on a fine sieve. It constitutes 78 per cent of the total proteids of wheat. It is made up of at least four components. The most abundant of these, **gluten-casein**, or **glutenin**, is a phytovitellin which remains as an insoluble residue on extraction of gluten with alcohol. The others, **gliadin**, **mucedin**, and **gluten-fibrin**, differ principally in their solubility in water and in alcohol of different degrees of concentration. Maize contains a protein, called **zein**, which resembles gluten-fibrin, but is not identical with it. It is insoluble in water, but soluble in alcohol, and in dilute alkaline solutions.

Histons—are obtained by decomposition of hæmoglobins and of nucleoproteids, or as addition products by union of protamins with albumins. They are therefore intermediate between the protamins and the other proteins, and closely related to the former. Neither histons nor protamins are "native albumins" in the sense that they exist in nature in their own form, but they are well-characterized proteins, which form component parts of more complex protein molecules which exist in nature. The histons are distinguished from other proteins chiefly by two properties dependent upon each other: their large content of hexon bases, and the basic character of the entire molecule.

The histons are soluble in water, from which they are precipitated by a small quantity of ammonia, the precipitates being soluble in excess, except ammoniacal salts be present, when they persist. Some histons do not conform entirely to the above (p. 588). They are readily soluble in acids. They are not coagulated by heat in pure aqueous solution, but in presence of salts they are coagulated, but not denaturated,

as the coagulum is soluble in acids, not as acid-albuminate, but as histon. They are precipitated by HNO_3 , but resemble the albumoses rather than the albumins in that the precipitate is redissolved on heating. They contain sulfur, but no phosphorus. They give the xanthoproteic and biuret reactions, but not the Millon. They contain no carbohydrate component. They have not been crystallized.

They resemble the protamins in that with solutions of albumins they form precipitates which are soluble in acids or alkalies; in that they form precipitates with phosphotungstic acid and other alkaloid reagents in solutions of neutral or faintly alkaline reaction, while the true native albumins only do so in acid liquids; and in their strongly basic character and high nitrogen content, a large proportion of which, as much as 40 per cent, separates as basic nitrogen on hydrolysis. Both histons and protamins have pronounced toxic action, causing first acceleration and then arrest of respiration, and marked diminution of blood pressure.

The described histons are: **Globin**, the "albumin component" of hæmoglobin (see Blood, p. 660). **Histon** occurs in its nucleic acid salt as the **nucleohiston** (p. 591) of the leucocytes of the thymus, and other glands, from which it is split by hydrolysing with BaH_2O_2 or dilute HCl . It is strongly basic, readily combines with acids, and is precipitated from its salts by ammonia, in an excess of which it is not soluble. **Parahiston**, also in the form of a nucleate, accompanies histon, the salts of the two bases apparently existing in combination, as they are in definite proportion in the nuclein derived from nucleohiston; **Salmon** is a histon from the spermatozoa of the salmon; **Scombron**, one from those of the mackerel, whose precipitate by ammonia is not redissolved by excess; and **Arbacion**, one from the testicles of the sea-urchin, which is only incompletely precipitated by ammonia.

Protamins.—These substances, which are regarded as the simplest of the proteins, have been obtained only from the melt (spermatozoa) of fishes, in which they exist combined with nucleic acids (p. 592). They contain no sulfur, but much nitrogen and little carbon. Their products of decomposition are much fewer in number than those of the proteins in general, yet they have many of the general reactions and properties of the proteins. They are alkaline, basic, nitrogenous substances, which can be salted out of their solutions by NaCl or $(\text{NH}_4)_2\text{SO}_4$ with more or less facility. They give the biuret reaction brilliantly, but not the Adamkiewicz, and, with the exception of cyclopterin, not the Millon reaction. They form salts with acids, which are soluble in water, insoluble in alcohol and in ether, of which the sulfate, picrate and platinochlorid are utilized for their extraction and purification. They are not coagulated by heat. Solutions of

their salts are precipitated in neutral or even alkaline solutions by phosphotungstic, tungstic, and picric acids, and by chromates and ferrocyanids. Probably their most characteristic reaction is the formation of precipitates of histones (p. 587) from ammoniacal solutions of albumins or of primary albumoses. On hydrolysis by boiling dilute acids, or by tryptic digestion they yield, first peptone-like substances, called **protones**, which are lævogyrous, and give the biuret reaction, but do not form histon precipitates with albumins in ammoniacal solution. Later more simple substances are obtained, among which the hexon bases, particularly arginin, predominate greatly, along with very small quantities of monamido acids, tryptophane and α -pyrrolidin carboxylic acid. A large proportion of their total nitrogen, 63-88 per cent, is basic. The described protamins are: **Salmin**, $C_{30}H_{57}N_{17}O_6$, from salmon melt, and **Clupein**, from the melt of the herring, were supposed to be identical, but, as they form different nucleates they are distinct substances (p. 591). On hydrolysis they yield 82-84 per cent of arginin, with a little amidovalerianic acid: **Scombrin**, $C_{32}H_{72}N_{16}O_8$, from the melt of the mackerel; **Sturin**, $C_{34}H_{71}N_{17}O_9$, from the melt of the sturgeon, which yields all three hexon bases, 13 per cent histidin, 58 per cent arginin, 12 per cent lysin, and an undetermined monamido acid; **Accipenserin**, $C_{35}H_{75}N_{18}O_9$, related to, but not identical with sturin, from another species of sturgeon; and **Cyclopterin** from the melt of the lump-fish, which yields 63 per cent of arginin, but no lysin or histidin, and 8 per cent of tyrosin, and gives the Millon reaction. Cyclopterin also differs from other protamins in containing sulfur.

The protamins are obtained from the melt, previously washed with alcohol-ether, by extraction with 1-2 per cent H_2SO_4 , precipitation with alcohol, and purification by repeated solution in water and precipitation with alcohol, and by conversion into the picrate or platinochlorid.

DERIVED ALBUMINS.

Albuminates.—Native albumins dissolve in very dilute acids or alkalies without immediate change, but with more concentrated acids or alkalies, or by prolonged contact with more dilute solutions, the native albumins behave as bases and acids, become denaturized, and form acid- or alkali-albuminates. The degree of concentration of acid required to produce the combination is greater than that necessary for alkalies, but a mineral acid of too great concentration causes coagulation. The formation of alkali-albuminate is also hindered by too great concentration of the alkali. In the formation of the albuminates the protein solution is converted into a more or less thick, transparent

jelly (Liederkühn's jelly), whose formation is accelerated by heat. The transparent "tata-albumen" obtained from alkalized hens' eggs is an alkali-albuminate (p. 584). Albuminates are soluble in dilute acids or alkalies, but insoluble in water or in solutions of neutral salts. They are therefore precipitated from their solutions by neutralization. Their solutions are not coagulated by heat.

The formation of alkali-albuminates is attended by loss of nitrogen (as NH_3), and of sulfur (as H_2S), and therefore, while acid-albuminate may be converted into alkali-albuminate by addition of alkali, the reverse change cannot be effected. Acid-albuminates are precipitated by very small quantities of neutral salts, the quantity of salt required being the less, the smaller the amount of acid present. During the gradual neutralization of a strongly acid solution of acid-albuminate a precipitate is alternately formed and redissolved, and finally remains permanent, because of alternate precipitation by the salt produced by neutralization of the acid, and resolution in the excess of acid. Alkali-albuminates are also precipitated by neutral salts, but it requires very much larger quantities of the salt to produce the result than with acid-albuminates. The fact that native albumins are only coagulated by heat in faintly acid solutions is explainable upon the theory that the already denaturized acid-albuminate is readily separated by the small quantity of salt present, while the alkali-albuminate, although denaturized, remains uncoagulated in presence of much larger amount of salts.

The formation of acid-albuminates is much accelerated by the presence of pepsin, and constitutes the first step in the process of gastric protein digestion, which process also rapidly proceeds further, with formation of albumoses and peptones, and even of more simple substances.

A form of acid-albuminate, called **syntonin**, is produced from the proteins of muscular tissue (p. 585) by the action of HCl of 2 p/m by prolonged contact, or by short contact of the same acid in presence of pepsin.

Albumoses and Peptones are products of digestion, and will be considered under that head.

Coagulated Albumins—are produced from some of the previously described proteins, either: (1) by heat; (2) by alcohol in presence of neutral salts. If the contact with alcohol be of short duration the protein is *precipitated*, and may be redissolved; if the contact be prolonged it is *coagulated* and permanently altered; (3) by long agitation of their solutions; (4) by the action of certain enzymes. But little is known of the nature of the change, or of the chemical characters of the products. These are white substances (fibrin, hard-boiled white of egg) insoluble in water, or in solutions of neutral

salts, or in dilute acids or alkalies at the ordinary temperature. They are soluble by conversion into acid- or alkali-albumins by concentrated acids or alkalies, or by the same when dilute if aided by heat. They are acted upon by digestive enzymes and converted into albumoses and peptones. Although coagulated albumins are usually artificial products, except fibrin naturally coagulated, proteins having similar properties are met with in the liver and in other glands.

PROTEIDS.

The proteins of this class are conjugate compounds, consisting of a native albumin united with some other well-defined "prosthetic" group (prosthetic=added). Thus, besides an albumin, the hæmoglobins on decomposition yield a crystalline pigment, the nucleoproteids a nucleic acid, and the glycoproteids a reducing carbohydrate.

Hæmoglobins.—(see Blood, p. 659).

Nucleoproteids—are compounds intimately connected with the processes of cell-life, which occur principally in glandular organs: liver, pancreas, thymus, kidneys, adrenal glands, mammary glands, etc., existing chiefly in the cell-nucleus, but also in the protoplasm. They are distinctly acid in function, are soluble in water and in dilute salt solutions, very soluble in alkalies, from which solutions they may be salted out by neutral salts. Their albumin component is coagulated by heat, by mineral acids, and by alkaloid reagents. Their solutions are dextrogyrous, while those of other proteins are lævogyrous, the left rotation being due to the nucleic acid component. They give the color reactions of the proteins.

The nucleoproteids are decomposed by heating with dilute acids, or by peptic digestion, into the products of hydrolysis of an albumin, and a "true nuclein." By continued decomposition the nuclein is decomposed into a further quantity of albumin product and a nucleic acid; and by still further decomposition the nucleic acid is split into xanthin and uracil bases, a phosphorus acid and a carbohydrate. The nucleoproteids of the melt of fishes are more simply constituted than those from mammalian tissues, and do not yield a nuclein as an intermediate product, but are directly split into a protamin or histon and a nucleic acid. These are, therefore, protamin or histon nucleates. Salmin nucleate contains 18.81 per cent nitrogen, and 7.55 per cent phosphorus; clupein nucleate, 21.07 per cent nitrogen, and 6.08 per cent phosphorus.

The best known of the nucleoproteids is **nucleohiston**, which is obtained from the leucocytes of the thymus, lymphatic glands, spleen and testicles, and from spermatozoa. When dry it is a white powder, soluble in water, in concentrated acetic and mineral acids, in solutions

of alkalies, and, when freshly precipitated, in solutions of NaCl or MgSO_4 ; insoluble in alcohol, methylic alcohol or dilute acetic acid. It contains 3.025 per cent phosphorus, and 0.701 per cent sulfur. Its solutions are dextrogyrous, $[\alpha]_D = +37.5^\circ$. When hydrolysed by heating with BaH_2O_2 or dilute HCl it yields histon (p. 587) and a nuclein, called **leuconuclein**. It is decomposed by alcoholic KHO, yielding an albumin and thymonucleic acid (p. 593). Nucleohiston, or the leuconuclein derived from it, is supposed to play an important part in the coagulation of the blood (p. 669).

Nucleins are obtained as insoluble or sparingly soluble residues on peptic digestion of the nucleoproteids. They contain 4-7 per cent of phosphorus, and traces of iron. They are colorless, amorphous, very sparingly soluble in water, moderately soluble in dilute alkalies, insoluble in alcohol and in dilute acids, not dissolved by peptic digestion, but dissolved by tryptic digestion. They behave as rather strong acids. They give the Millon and biuret reactions, and readily take up basic dyes from aqueous or alcoholic solutions. They are coagulated by heat. They are more strongly dextrogyrous than the nucleoproteids.

On hydrolysis by boiling dilute acids they yield albumin products and nucleic acids, which latter are further decomposed, yielding xanthin and uracil bases, a carbohydrate and metaphosphoric acid. Inversely, compounds having the properties of nucleins are produced by precipitating solutions of albumins with nucleic acids. As they still contain albumins, they do not differ essentially from the nucleoproteids, but are rather to be considered as nucleoproteids more rich in phosphorus, poorer in nitrogen, and more strongly acid than the native nucleoproteids, and as transition products between the nucleoproteids and the nucleic acids.

Nucleic Acids—also called *nucleinic acids*, are products of decomposition of nucleoproteids by alkalies, either directly or through the nucleins. They are amorphous, white, sparingly soluble in water, easily soluble in alkalies; insoluble in alcohol and in ether. They are precipitated from their solutions by mineral acids, including phosphotungstic, by alcohol, and by $(\text{NH}_4)_2\text{SO}_4$ in presence of acetic acid, but not by acetic acid alone, except guanylic acid. Their solutions form precipitates (of nucleins) with acid solutions of albumins. They give the xanthoproteic and Adamkiewicz reactions, but not the biuret or Millon. They are dibasic acids, forming acid and neutral salts.

On hydrolysis the nucleic acids yield xanthin and uracil bases, phosphoric acid, and a carbohydrate as final products. All of the four xanthin bases have been obtained from nucleic acids. It is believed that there exists a distinct nucleic acid corresponding to each xanthin base, a **xanthylic**, a **hypoxanthylic** (*sarcylic*), a **guanylic**, and an **adenylic acid**, although but one of these, guanylic acid, has been

obtained in a condition of purity. As, however, certain nucleoproteids on hydrolysis yield more than one xanthin base, and some as many as three, it is possible that nucleic acids may exist, whose molecules contain more than one xanthin base. Nor does the hydrolysis of the nucleoproteids or nucleic acids proceed to the final result in a single stage. From the parent nucleoproteid a nucleic acid is first split off, designated as an α -acid, which is very sparingly soluble, and whose solutions gelatinize if they contain 5 per cent or more of the acid. By the action of KHO about two-thirds of the total xanthin bases are split off, and a β -acid, probably an inferior polymere, is obtained, which is more soluble than the α -acid (but see guanylic acid, below), and whose solutions do not gelatinize. By the continued action of the alkali this acid splits off the remainder of the xanthin bases and cytosin (p. 525), leaving **thymic acid**, which then, by further hydrolysis, yields thymine (p. 524), a carbohydrate, phosphoric acid, and other undetermined products. The carbohydrate component is most frequently a pentose, giving Tollens' reaction (p. 323), sometimes a hexose; and sometimes lævulinic acid (p. 347) is the carbohydrate representative. Thymic acid is quite soluble in water, and is not precipitated by mineral acids. Its solutions form precipitates in acid solutions of albumins.

Two **guanylic acids**, $C_{44}H_{66}N_{20}P_4O_{34}$, are obtained from the pancreas: the α -acid, easily soluble in cold water, contains 6.65 per cent phosphorus and 15.38 per cent nitrogen. By the action of alkalis it splits off a pentose, l-xylose, and forms β -guanylic acid, soluble in hot water, less soluble in cold water, containing 7.64 per cent phosphorus and 18.21 per cent nitrogen, which appears to be an ester of a polyglycerophosphoric acid. By hydrolysis it yields four molecules of guanin, three of pentose, and three of glycerol for each four atoms of phosphorus, but no other xanthin base and no pyrimidin derivative. In it $P:N::4:9.5$.

Two **thymonucleic acids**, $C_{40}H_{56}N_{14}P_4O_{26}$, have been obtained from the thymus, to one of which the nucleic acids from the melt of sturgeon, salmon and herring are closely related, if they be not identical. They yield 23 per cent P_2O_5 , and $P:N::4:14$. They are hydrolysed by heating with water, yielding adenine, guanin and thymic acid; and, on deeper hydrolysis by H_2SO_4 , guanin, adenine, thymine, cytosine, and lævulinic acid, but no carbohydrate.

The two principal nucleic acids of vegetable origin, **triticonucleic acid**, $C_{41}H_{61}N_{16}P_4O_{31}$, from wheat, and **yeast nucleic acid**, are, if not identical, closely related. On hydrolysis by acids they both yield one molecule each of adenine, guanin and cytosine, two of uracil, and three of pentose for each four atoms of phosphorus. Yeast nucleic acid is also said to yield a hexose.

Glycoproteids—are proteins which on hydrolysis by dilute mineral acids yield a notable quantity of a substance capable of reducing Fehling's solution, but no xanthin base. Because of their carbohydrate content these substances contain a smaller proportion of nitrogen and of carbon, and a larger proportion of oxygen than other proteins. They include the **mucins** and **mucoids**, the distinction between which is not sharply drawn. They exist in the saliva, bile, nasal mucus, vaginal mucus, cornea, vitreous, tendons, cartilage, umbilical cord, and the fluid of ovarian cysts.

When dry they are white or gray, soluble in much water, to acid solutions, which are not coagulated by heat. In presence of a trace of alkali the solution assumes a viscous, stringy character, which is more pronounced with the mucins than with the mucoids, this, and some differences in the conditions of precipitation, being the only distinctions between the two. If the alkaline solution be heated the proteids dissolve as alkali-albuminate. The glycoproteids are precipitated from their aqueous or cold alkaline solutions by acetic acid, the precipitate being insoluble in excess of acid. They are also precipitated by alcohol. They are insoluble in dilute acids, but if they be heated with dilute mineral acids, they dissolve as acid-albuminates or albumoses, the liquid turns brown, and is capable of reducing Fehling's solution. They are dissolved very slowly by peptic or tryptic digestion. On hydrolysis they yield 30–37 per cent of a carbohydrate, which is usually glucosamin (p. 387), which probably exists in the parent substance as a nitrogenous polysaccharid.

Cartilage contains a mucoid, called **chondromucoid**, which on hydrolysis by dilute mineral acids yields albumin products and an ester-sulfuric acid, called **chondroitin-sulfuric acid**, or **chondroitic acid**. This acid exists in cartilage and in urine, and has the empirical formula, $C_{18}H_{27}NSO_{17}$. On hydrolysis it first splits off H_2SO_4 and yields **chondroitin**, $C_{18}H_{27}NO_{14}$, a gummy, monobasic acid, which on further hydrolysis splits off acetic acid, and yields **chondrosin**, $C_{12}H_{21}NO_{11}$, also a gummy, monobasic acid, soluble in water, which reduces Fehling's solution more energetically than does glucose, and is dextrogyrous. On further hydrolysis chondrosin yields a tetra-oxyamidocaproic acid, $C_6H_{13}NO_6$, and an undetermined carbohydrate component. Chondroitin-sulfuric acid is a white, amorphous powder, very soluble in water, as are its salts. Its neutral solutions are precipitated by $SnCl_2$, $PbOPb(C_2H_3O_2)_2$, Fe_2Cl_6 , and alcohol. Solutions of its alkali-metal salts cause precipitates in solutions of albumins or of gelatin.

The fluid of ovarian cysts contains a pathological glycoproteid, called **metalbumin**, or **pseudomucin**, which forms a viscid, stringy solution, which becomes opalescent, but does not coagulate, on being

heated, and is precipitated by alcohol, but which differs from solutions of other glycoproteids in not being precipitated by acetic acid. **Paralbumin**, also from ovarian cysts, is apparently a mixture of pseudomucin with albumins.

ALBUMINOIDS.

The albuminoids are proteins which are insoluble in the neutral solvents of the albumins or proteids. They can only be dissolved after undergoing chemical change. They are of denser consistency than the other proteins, and, while the albumins and proteids are constituents of the nutrient fluids or of the nuclei or protoplasm of the cells, the albuminoids occur in skeletal, connective, and epidermal tissues. The albuminoids are also much more resistant than other proteins to the action of decomposing agents, but, when decomposed, they yield the same kind of decomposition products as do the other proteins, except that certain groups, such as the tyrosin and indole complexes, are absent, while other groups are produced in larger amount.

Keratins—are the albuminoids most closely allied to the albumins. Indeed, they are sometimes classed as true albumins, because of the large proportion of sulfur which they contain; the presence in them of a carbohydrate component; and the occurrence among their products of decomposition of arginin, tyrosin and phenylalanin, the first of which contains the guanidin remainder and the last represents the indole complex, which are present in the albumins, but usually absent in the albuminoids.

The keratins occur in epidermis, hair, nails, horn, hoofs, feathers, tortoise-shell, and other epidermic tissues, in brain and nerve tissue (**neuro-keratin**), and in the membranes of eggs. They vary in composition: Hair keratin contains 16.80 to 17.14 per cent nitrogen and 4 to 5 per cent sulfur; and neurokeratin 11.46 per cent nitrogen and 1.87 per cent sulfur. The maximum of sulfur is in the keratin of human hair, which yields up a portion of its sulfur very readily, forming H_2S even with boiling water, a fact which is utilized in lead and other metallic hair dyes. The keratins are amorphous, insoluble in water, alcohol, ether, acids, gastric juice, or trypsin, slowly soluble in alkalis. When heated with water under pressure to 150° – 200° , they dissolve, but do not gelatinize. They give the xanthoproteic and Millon reactions, sometimes imperfectly. Horn and hair on decomposition yield alanin, α -amidovalerianic acid, leucin, aspartic acid, serin, tyrosin, arginin, lysin, phenylalanin, and α -pyrrolidin carboxylic acid as nitrogenous split products. Most, if not all, of the sulfur is obtained as cystin: from horn 6.8 per cent, and from human hair 13.92 per cent.

Albumoid is a substance intermediate between the keratins and

the albumins, obtained from tracheal cartilages. It is soluble in gastric juice, but in other respects resembles the keratins.

Collagen—is the principal constituent of connective tissues, bones (osseïn), tendons and cartilage. In the last named it exists in combination with chondroitin sulfates (p. 594). When dry it is amorphous, yellowish, hard, and insoluble in water, or dilute acids or alkalies. When macerated with cold dilute acids it becomes pliable. The tannins combine with collagen to form a tough, hard, imputrescible material, which constitutes leather. Collagen, when heated with dilute acids, or with water under pressure, is converted into **gelatin**, which appears to be a hydrate of the parent substance. Glue is an impure form of gelatin. Gelatin is amorphous, yellowish, hard, brittle, swells, but does not dissolve, in cold water, and at 30° forms a solution with water, which solidifies to a jelly-like mass on cooling, and liquifies when warmed. Gelatin and collagen give the xanthoproteic and biuret reactions, but not the Millon or Adamkiewicz. When hydrolysed by acids they yield the usual decomposition products of the proteins, except that they yield no tyrosin, indole, or cystin. They do, however, contain sulfur, and also an aromatic complex in small amount, as they yield 0.4 per cent of phenylalanin. They yield glycocoll in large amount, 16.5 per cent, and smaller quantities of alanin, leucin and other monamido acids and diamido acids (2.5 per cent arginin). They contain no carbohydrate component. Collagen, if previously heated with water to 70° , and gelatin are dissolved by peptic or tryptic digestion with formation of **gelatoses** and **gelatin-peptones**, which are diffusible, and during whose formation a considerable amount of glycocoll separates. These digestion products of gelatin are not identical with those derived from the true albumins (p. 619), and gelatin is capable of only partially replacing albumins in a dietary. **Isinglass**, a colorless, transparent gelatin from the swimming bladders of certain fishes, and gelatin made from cartilage differ from ordinary gelatin in being completely soluble in water. They contain chondroitin sulfates as well as gelatin.

Elastin—occurs in elastic tissues, notably the ligamentum nuchæ. When dry it is a yellow powder, insoluble in neutral solvents, only slowly soluble in boiling, concentrated KHO, or concentrated H_2SO_4 , soluble in hot HCl. It contains 0.27–0.66 per cent of sulfur, which is completely split off by NaHO. It gives the xanthoproteic, biuret, Millon and Adamkiewicz reactions after solution by NaHO. On hydrolysis it yields notable quantities of leucin, 45 per cent, smaller amounts of other monamido acids, and very small quantities of tyrosin, 0.25 per cent, and of diamido acids 0.3 per cent, but no indole or skatole. By the action of proteolytic enzymes it yields two albumoses, both soluble in water, one, **protoelastose**, precipitable by heat, by

mineral acids, or by acetic acid and ferrocyanid, the other, **deutero-elastose**, not so precipitable.

Other albuminoids are: **Reticulin**, from connective tissues, intestinal mucous membrane, liver, spleen, kidneys, lungs; contains phosphorus. **Spongin** is the principal organic constituent of sponges. **Conchiolin** is the albuminoid of the shells of molluscs, **Fibroin** and **sericin** are the principal constituents of raw silk. **Kornein** is obtained from coral zoöphytes. **Ichthylepidin** exists, along with collagen, in fish scales. **Chitin** constitutes the organic portion of the hard parts of insects and crustaceans. It probably is not a protein, but a nitrogenous polysaccharid, whose product of hydrolysis is glucosamin, or chitoseamin.

Amyloid—is a purely pathological product which appears as the *corpora amylacea*, resembling starch granules in gross appearance, or deposited in masses in amyloid degeneration of the parenchyma of the liver, kidneys, spleen, etc. It is white, amorphous, insoluble, except in concentrated acids and alkalies, and only slowly dissolved by peptic or tryptic digestion. It gives all of the protein color reactions. On hydrolysis it yields 3.9 per cent tyrosin, leucin and aspartic and glutamic acids. It contains no carbohydrate component, but does contain a chondroitin sulfuric acid complex. It is colored brown-red by iodine, changing to violet on addition of H_2SO_4 ; and is colored bright-red by eosin, rose-red by anilin violet, and red by anilin green.

Melanins—are dark-colored substances occurring in hair, choroid, iris, skin of the negro, and in melanotic tumors. The melanoidins which remain in the humus fraction (p. 580) on decomposition of proteins are related to them, and their percentage composition is similar to those of the proteins. They are certainly protein derivatives, if they be not albuminoids. Some contain sulfur and iron, others do not. Their content of nitrogen varies from 8.5 to 12.3 per cent, of sulfur from 0 to 10 per cent, and of iron from 0 to 2.7 per cent. When dry they are brown or black, amorphous, insoluble in neutral solvents, and in dilute acids; soluble in concentrated acids, and readily soluble in alkalies. They do not give the protein color reactions. Indole and skatole have been obtained as products of their hydrolysis, but neither tyrosin or other amido acids.

CHEMICO-PHYSIOLOGICAL PROCESSES.

One of the most striking differences between unorganized and organized nature is that in the former those changes which occur are almost entirely physical, while in the latter they are essentially chemical. Water passes through the conditions of solid, liquid and vapor,

the rocks are eroded, the air varies in temperature and moves from place to place, all physical changes, but neither water, rock nor air suffers change of composition. But in vegetable and animal bodies changes in composition are constant and essential to life; the atoms of carbon, hydrogen, nitrogen and oxygen are in constant passage from one form of combination to another. Indeed life may be said to consist of chemical reactions; and the physical processes and conditions of and in the bodies of vegetables or animals occur or exist that these reactions may take place.

Energy, like matter, is indestructible, and cannot be created. The sum of potential and kinetic energy in the universe is immutable. The relative proportions of the two forms of energy is constantly varying. Every chemical change involves the conversion of potential into kinetic energy, or the reverse. The atoms of carbon and oxygen uncombined with each other, are endowed with a definite amount of potential energy, which is converted by their union into a definite and equivalent amount of kinetic energy, which is manifested and is measurable as heat, which may in turn be converted into other forms of energy. Once united, the carbon and oxygen have lost the potential energy which they possessed while ununited, and, as energy cannot be created, they can only recover it by some second reaction in which an equivalent quantity of kinetic energy becomes potential in separating the atoms once more. This cycle may be mathematically expressed by the equations: $C + O_2 + \text{potential} = CO_2 + \text{kinetic}$, and $CO_2 + \text{kinetic} = C + O_2 + \text{potential}$. As animal bodies are constantly converting potential energy into the kinetic forms of heat, motion, etc., they must be supplied with potential energy from without, which, in its turn, has been derived from some form of kinetic energy.

The source of this energy is the kinetic energy of the sun's rays. The green parts of plants owe their color to the presence of a pigment called **chlorophyll**, which is only present in leaves and stems exposed to sunlight. In the daytime, and while exposed to sunlight, plants absorb carbon dioxide from the air and give off oxygen; during the night they absorb oxygen and evolve carbon dioxide; but in very much less quantity. Plants also absorb water and ammonia. From these comparatively simple substances the plants form carbohydrates and proteins under the influence of the kinetic energy of the sun's rays, which thereby becomes potential. In the animal body the carbohydrates and proteins are converted into carbon dioxide, water and urea (the last-named yields ammonia by fermentation) and their potential energy becomes kinetic. The tissues of the plant are, directly or indirectly, the food of the animal, and the excreta of the animal constitute the food of the plant. The chemical processes in

the vegetable are essentially synthetic, producing complex substances from simpler forms of combination; but analytic processes also occur in vegetables, as that which results in the evolution of oxygen, above referred to. The processes of animal-nature are, on the other hand, essentially analytic, complex combinations being reduced to simpler forms; but synthetic processes also occur in animal bodies, as in the formation of hippuric and the ester-sulfuric acids.

The composition of various articles used as foods, the effects upon them of different methods of preparation, and the relative proportions in which the several components should be contained in properly adjusted dietaries, are, like the composition of air under varying conditions, important subjects of inquiry for the hygienic chemist. In this place, however, we will content ourselves with the statement that the materials required for the chemical processes taking place in the body, and contributing to the growth or repair of the tissues, and to the production of kinetic energy, are of six classes: (1) Oxygen, (2) water, (3) mineral salts, (4) carbohydrates, (5) fats, (6) proteins. Of these, oxygen, water and salts pass into the system by the physical processes of diffusion and absorption, without the necessity of any preliminary chemical treatment. But the fats, the carbohydrates, and, notably, the proteins, require chemical modification from the forms in which they are taken into the mouth before they can be absorbed. This is the purpose of digestion.

Chemical processes occurring in the body may therefore be divided into the two classes of preparatory and essential. The former including the processes preparatory to absorption which occur in the alimentary canal; the latter the metabolism of the tissues, cells, and fluids of the body.

FERMENTS AND ENZYMES.

Since the historic researches of Pasteur, and until quite recently, the name **ferment** has been applied to certain microörganisms: mould fungi, yeast fungi and bacteria, which by their growth cause definite chemical changes in certain substances contained in the media in which they develop. **Enzymes** are more or less hypothetical substances, some of which are derived from the microörganisms above referred to, all produced by living cells, and exert their characteristic actions. There is at present a tendency to use the terms ferment and enzyme synonymously to apply to the latter, which is to be regretted, even if all ferments be shown to act by producing enzymes, as, if followed, it causes a useless multiplication of names on the one hand, and, on the other, leaves the important class of organized ferments generically nameless.

Alcoholic fermentation as conducted by brewers and distillers is the result of the metabolic processes in the growth of the yeast plant, during which glucose is consumed and carbon dioxid and alcohol are eliminated. Brewers' yeast is a fungus, *Saccharomyces cerevisia*, which forms rounded or elongated cells, whose greatest diameter is 8-10 μ and which propagates by budding. Two varieties of this plant exist, corresponding to the "low yeast," which sinks to the bottom of the fermenting liquid, and the "high yeast," which rises to the surface. Vinous fermentation is usually produced by *S. elipsoideus*, but also by *S. apiculatus* and *S. Pasteurianus*, which exist upon the skins of grapes and other fruits. *S. cerevisia* produces alcoholic fermentation not only of glucose, but also of saccharose and maltose, which involves the preliminary inversion of these disaccharids. Certain other yeasts behave differently with sugars other than glucose: *S. apiculatus* does not ferment (invert) either maltose or saccharose; *S. octosporus* and *S. membranefaciens* ferment maltose but not saccharose; *S. Marxianus* and *S. Ludwigii* ferment saccharose but not maltose. Of the monosaccharids only the dextro sugars containing C_3 or a multiple thereof are fermentable. Glyceric aldehyde and the d-hexoses are fermented by yeast; the l-hexoses, pentoses, heptoses and ostoses are not. The disaccharids, saccharose, lactose and maltose, and the trisaccharid, raffinose, only ferment after inversion.

The most favorable temperature for the action of yeast is 24°. At 55°-60° the life of the plant is destroyed. It is also killed by microbic poisons, such as chloroform, thymol, toluol, carbolic acid, boric acid, mercuric chlorid, etc. The action is also arrested by accumulation of the product when the proportion of alcohol reaches 20 per cent. Ethyl alcohol is by no means the only product of yeast fermentation; aldehyde, normal propylic, isobutylic and isoamylic alcohols, ænanthylic ester, isobutylene glycol, glycerol, acetic and succinic acids, and furfurole are also formed.

Certain mould fungi also cause alcoholic fermentation. Thus *Mucor mucedo*, *M. alternans*, *M. racemosus*, *Amylomyces Rouzii* produce alcohol not only from glucose but also from dextrins and from hydrated starch when growing submerged in the liquid. *Eurotium orizæ* is an aspergillus used by the Japanese to ferment rice in the preparation of "sake."

The selective action, above referred to, which yeast and other ferments exhibit toward optical isomeres has been explained (Fischer) by the supposition that the enzymes by which their action is produced (below) themselves possess a stereochemical configuration (p. 311) which permits of their adaptation with a sugar whose conformation is receptive, but not with its stereoisomere, the spatial arrangement of whose parts is obstructive to such interunion. A similar selective

action is exerted by certain mould fungi, such as *Penicillium glaucum* (the common blue mould) and *Aspergillus niger*, whose selective power is utilized for the separation of one optically active modification from a racemic form. Thus when these moulds are grown upon inactive ammonium lactate only the dextrolactate remains. They also exert a selective action between other stereoisomeres. Thus in a mixture of fumaric and maleic acids they consume the former and leave the latter.

Bacterial fermentations occur in great variety. The slimy material known popularly as "mother of vinegar" is formed of *Bacterium aceti*, which in its growth causes **acetous fermentation** in weak alcoholic liquids, by oxidizing ethylic alcohol to acetic acid. **Butylic fermentation** is produced by *Bacillus butylicus*, which splits glycerol, monosaccharids, disaccharids, dextrin, and starch with formation of normal butyl alcohol and small quantities of isobutyl alcohol. Possibly the formation of the higher alcohols in ordinary alcoholic fermentation may be due to the presence of this and other bacteria in the yeast. **Butyric fermentation** is set up by a variety of bacteria, notably by *Bacillus amylobacter*, which exists in soils, river waters, hay, etc., and in the intestine. The formation of butyric acid is sometimes directly from the carbohydrate: $C_6H_{12}O_6 = C_4H_8O_2 + 2CO_2 + 2H_2$, and sometimes with intermediate formation of lactic acid: $C_6H_{12}O_6 = 2C_3H_6O_3$. **Lactic fermentation** is produced by a number of species of bacteria. In the souring of milk, in which the lactose is first hydrolysed, and its constituents then split to lactic acid, *Bacillus acidi lactici* is usually the most active. It produces the racemic acid, along with formic and acetic acids, alcohol, carbon dioxid and hydrogen. The growth of this bacterium is most active at 35° – 45° , and is arrested by slight excess of free acid. Therefore a better yield is obtained in presence of $CaCO_3$ to neutralize the acids formed. It also causes lactic fermentation of glucose and of saccharose. *Bacterium coli commune* causes lactic fermentation of both glucose and saccharose, and produces d-lactic acid. The typhoid bacillus ferments glucose but not saccharose, and produces l- and r-lactic acids. Mixed lactic and alcoholic fermentations are set up by lactic and alcoholic ferments growing in the same medium. Thus in the manufacture of "kéfir," an alcoholic beverage made from milk, *Bacillus caucasicus* and *Saccharomyces kéfir* are simultaneously in action. The **ammoniacal fermentation** of urine, in which urea is hydrolysed to carbon dioxid and ammonia by the action of *Micrococcus ureæ*, is one case of a great variety of bacterial fermentations of nitrogenous material, including putrefaction, the nitrification of natural waters, etc., which result in the decomposition of complex molecules to the simpler forms in which nitrogen and carbon may be utilized as plant-food. It is highly probable that diseases

of bacterial origin are the manifestations of the action of specific poisons, formed as fermentation products by the bacteria.

Sucrase—Maltase—Zymase.—It has been long known that a filtered extract of certain yeasts made with thymolysed water is capable of inverting cane-sugar, and that similar extracts from other yeasts hydrolyse both saccharose and maltose. From which it may be inferred that certain yeasts produce a non-organized substance, soluble in water, which is capable of inverting saccharose, and which is called **invertin**, or **invertase**, or **sucrase**; and that other yeasts secrete, besides sucrase, another similar material, called **maltase**, which hydrolyses maltose. But, although the chief function of yeast is the production of alcohol, no soluble substance is obtainable from it by mere extraction with water, which causes alcoholic fermentation. Quite recently Buchner, by grinding yeast with fine sand and kieselguhr, by which treatment the yeast cells are ruptured, and then subjecting the mass to great pressure, obtained a liquid which, after thorough filtration, readily produces alcohol and carbon dioxid from saccharose. This liquid therefore contains, besides the sucrase above mentioned, another soluble substance, called **zymase**, capable of splitting glucose to alcohol and carbon dioxid. And, as this latter agent can only be obtained after rupture of the yeast cells, it may be considered as demonstrated that these cells produce two kinds of active substance, one, the sucrase or maltase, which it excretes to perform its function in the medium external to the cell, and the other, the zymase, which acts within the cell.

Sucrase exists in all *Saccharomyces* capable of fermenting cane-sugar (not in *S. octosporus*, *S. membranæfaciens*, or *S. apiculatus*), in many mould fungi (*Penicillium glaucum*, *Aspergillus niger*, *A. oryzae*, *Mucor racemosus*, etc.), in certain cells of germinating seeds of higher plants, in the bodies of bees, and in the intestinal mucous membrane and liver of higher animals. An active preparation of sucrase is obtained by Osborne's method: 500 gm. of yeast are rubbed up with 500 cc. of 96 per cent alcohol, and the mixture allowed to stand 24 hours. The alcohol is then filtered off and the residue macerated in 500 cc. of chloroform water for six days at 30°–35°. The aqueous liquid is then filtered into 96 per cent alcohol, and the flocculent precipitate washed with absolute alcohol, and dried in vacuo over sulfuric acid. The product still contains a notable quantity of salts, which may be in great part removed by frequent agitation of 20 gms. of the material with 500 cc. of water, treatment with ammonia to precipitate earthy phosphates, filtration, dialysis, concentration to small volume in vacuo at 30°, reprecipitation by alcohol, and drying in vacuo.

Sucrase hydrolyses saccharose and raffinose, but neither maltose

nor lactose. In the dry state it may be heated to 160° without deterioration, but when moist it is slowly destroyed at 45° . It acts most energetically at 55° . A small quantity of acid favors its action, but larger amounts impede it, as do alkalies in small amount.

Maltase exists in yeasts (not in *S. Marxianus* or *S. Ludwigii*) and in mould fungi, and is widely disseminated in the animal economy, in saliva, intestinal juice, pancreas, liver, lungs, lymphatic glands, spleen, kidneys, testicles, blood, urine, and bile. It is best obtained from maize by extraction with water containing alcohol and tartaric acid, and precipitation by alcohol. Maltase obtained from yeast and those of animal origin differ in certain of their actions, thus the former saponifies α -methyl glucosid, which the latter do not. Chloroform hinders the action of maltase, but is indifferent to sucrase and to most of the agents of this class.

Zymase is unstable in solution, but retains its activity when the extract is evaporated to dryness in vacuo at 20° – 25° . Or the precipitate formed in its aqueous solution by alcohol may be similarly dried. It acts best at 22° , and in solutions containing 16 per cent of sugar. Small quantities of acids arrest its action, which is favored by small quantities of alkalies. Its action is also arrested by hydrocyanic acid and by formic aldehyde.

Enzymes.—Sucrase, maltase and zymase are representatives of a numerous class of agents which play important rôles in vegetable and animal life, and which are called **enzymes**, or **zymases**, or **soluble ferments**. The general characteristic of these agents is that they are capable of causing change in a large amount of the materials upon which they exert their specific actions, while they themselves remain unaltered. Thus it is claimed that pepsin can digest 500,000 times its weight of fibrin, and be recovered, still active, from the solution. They are soluble in water and in glycerol, and are precipitated from these solutions by alcohol, or by salting out from aqueous solution by ammonium sulfate. Prolonged contact with alcohol destroys the activity of most enzymes, but not of all. For each there is a definite temperature which is the "temperature optima" at which the action is most energetic; and all are destroyed at 75° – 80° . Each produces its best action only in a medium of a certain reaction. Thus pepsin acts well only in an acid liquid, trypsin only in one which is alkaline. The action of all enzymes is hindered by accumulation of their products. The presence of certain substances, most of which are poisonous to the higher animals and all of which are destructive to the organized ferments, inhibit the action of enzymes. Such are mercuric chlorid, carbolic acid, hydrocyanic acid, etc. The action of most enzymes is hydrolytic in character, as in the splitting of di- and polysaccharids, the saponification of fats, the decomposition of urea, and the splitting

of the glucosids, but there are some which produce oxidations, as laccase and tyrosinase, or simple decompositions, as zymase; indeed, there appears to be no limit to the possibilities of their actions. Their actions do not proceed to completion, at least in some cases, and therefore it is theoretically probable that the reactions are reversible (p. 89). In fact, in the action of maltase upon maltose it has been shown that when a certain proportion of glucose has been produced the action ceases, and that if glucose be then removed the hydrolysis of maltose continues, but if glucose be added maltose is produced. The latter action is clearly synthetic, and it is also probable that the synthetic formation of hippuric acid in the kidney is due to enzyme action. Some enzymes are produced in cells from which they are excreted to act in the surrounding media, as sucrase and pepsin; others act within the cells in which they are produced, as zymase and the several autolytic enzymes. Enzymes in general decompose hydrogen peroxid with liberation of oxygen, but, as a temperature of 60° destroys this power, frequently without affecting the characteristic action of the enzyme, the decomposition of hydrogen peroxid may be due to foreign substances, although such cannot be the case with colloidal platinum (below). Certain cells produce, not the enzyme itself but a precursor, a **zymogen**, or **proenzym**, from which the enzyme is developed by secondary action. Thus pepsin and thrombin are formed from pepsinogen and prothrombin. Most enzymes may be extracted by water, to which thymol or chloroform is added to prevent bacterial action, or by glycerol. Another method of their separation from aqueous solution is by the formation therein of a precipitate of calcium phosphate, or other indifferent insoluble substance, which carries the enzyme down mechanically. The precipitate is then washed, dissolved in dilute hydrochloric acid, and the solution subjected to dialysis.

Concerning the chemical nature of the enzymes nothing is known with certainty, as no enzyme has yet been obtained in a condition approaching purity. It has been supposed that they are proteins, from their instability, their precipitation by salting and by alcohol, the apparent nitrogen content of some of them, and their non-diffusibility. But it is by no means certain that some at least of them contain any nitrogen. It has been suggested (Arthus) that they are not individual substances, but conditions of some existent substance or substances. This view is supported by the discovery by Bredig and V. Berneck of "mineral enzymes." If an electric arc be passed between platinum points under water a dark-brown "colloid solution" is obtained, containing metallic platinum in a state of extremely fine subdivision. This colloid platinum exhibits the action of an enzyme in decomposing hydrogen peroxid energetically and in very large amount, and such action is modified by various agencies in the same ways as is

that of an enzyme. There is a temperature optima, and complete arrest of the action by heat, a diminution of action with increase of alkalinity, and arrest of action by hydrocyanic acid. Moreover, very finely divided platinum, osmium, iridium, or silver bring about the inversion of cane-sugar at elevated temperatures.

Whatever may be the nature of the enzymes, whether they are definite and distinct chemical individuals, or peculiar physical conditions of certain well-defined substances which are inert in this regard under other conditions, it is certain that soluble products are obtainable from certain cells which are capable of being concentrated to a certain degree, although not as yet separable in a pure form, and which exert powerful and well-defined actions. It is therefore convenient, provisionally at all events, to speak of these substances as if they were definite entities. There seems, however, to exist a tendency to abuse the privilege of this rather easy method of explaining chemical actions observed in living beings, and to immediately name a new enzyme as the cause of any unexplained or newly discovered decomposition.

In naming an enzyme, the rule is adhered to as far as possible of giving it the name of the substance which it acts upon, modified by changing the termination to *ase*; as amylase, maltase, urease, etc. To this rule we have, however, exceptions, such as pepsin, amylopsin, emulsin, etc.

The enzymes are classified according to the nature of their actions and that of the substances acted upon:

1. *Amylolytic enzymes*—which hydrolyse starch through the stages of amyloextrin, erythroextrins, and achrooextrins to maltose, an action frequently referred to as **diastatic**. These enzymes are widely distributed in nature. Prominent among them are the **amylase**, or **diastase** produced during the germination of grain, and the diastatic enzymes of the saliva and pancreatic secretion. In this class are also included enzymes which hydrolyse carbohydrates more or less closely allied to starch: the hepatic enzyme which converts glycogen into glucose, **cellulase**, which hydrolyses cellulose, **inulase**, which converts inulin into fructose, etc.

2. *Invertases*—which hydrolyse disaccharids, or the trisaccharid raffinose, to their constituent monosaccharids. They are **sucrase**, **maltase** and **lactase**. Inverting enzymes are not active in the salivary, gastric or pancreatic secretions, but are in the intestinal juice.

3. *Lipolytic enzymes*—which saponify fats to fatty acids and glycerol. **Lipases** exist in many vegetables, *Ricinus*, *Papaver*, hemp seeds, maize, mould fungi, etc., and in the gastric and pancreatic secretions.

4. *Proteolytic enzymes*—which cause the hydrolytic decomposition of albumins to albumoses, peptones, and simpler compounds. They

include pepsin, trypsin, the papayotin of *Carica papaya*, and the autolytic enzymes which exist in various organs and cause their aseptic autolytic digestion after death.

5. *Glucosid-splitting enzymes*—such as **emulsin**, which hydrolyses amygdalin to glucose, benzoic aldehyde and hydrocyanic acid, and **myrosin**, which splits potassium myronate to glucose, allyl isothiocyanate and potassium sulfate.

6. *Oxidases*—which cause oxidations. The best known of these is **laccase**, which causes the oxidation of laccol, an oily liquid possessed of poisonous qualities, obtained from the Japanese lac tree, to a hard, brilliant, black pigment. Laccase also occurs in many other plants; beets, carrots, potatoes, asparagus, grasses, apples, etc. It also oxidizes aromatic compounds containing two OH, or an OH and an NH₂ group in ortho or para positions. Thus it converts hydroquinone and para-amidophenol into quinone. **Tyrosinase**, which also occurs in many plants, beets, potatoes, dahlia, fungi, etc., causes oxidation of tyrosin with formation of red and black derivatives, and also oxidizes other phenolic compounds. Laccase has no action upon tyrosin. **Oenoxydase**, which causes the oxidation and precipitation of the coloring matters of French and Italian wines. Numerous other oxidases have been named as the causes of oxidations occurring in animal bodies; although their existence cannot be said to have been demonstrated. Such are the **glycolytic enzymes** said to cause the oxidation of glucose in the liver and blood, oxidases in the liver and spleen causing oxidation of xanthin and hypoxanthin to uric acid, others oxidizing benzoic and salicylic aldehydes to the corresponding acids, still others oxidizing the tartrates, citrates and malates to carbonates, etc.

7. *Coagulating enzymes*—which bring about the formation of fibrin and of myogen and myosin fibrin, and the coagulation of casein.

8. *Ureases*—which cause the hydrolysis of urea to carbon dioxide and ammonia, are produced by *Micrococcus ureæ*, *Bacterium ureæ*, *Bacillus fluorescens*, and numerous other bacteria. *Micrococcus ureæ* also causes the hydrolysis of hippuric acid to glycocoll and benzoic acid.

Numerous other enzymes have been named as causing decomposition of nucleic acids, the conversion of cystin into taurin, the conversion of amido acids to amids, the deamidation of guanin and adenin, etc., etc.

DIGESTION.

SALIVA.

The saliva is a mixture of the secretions of several glands: The **submaxillary saliva**, which may be obtained by inserting a canula in Wharton's duct, is a clear, thin, colorless, slightly viscid, frothy,

alkaline liquid; sp. gr. 1002 to 1003; containing 3.6 to 4.5 p/m of solids. These solids consist of mucin, a trace of albumin, a diastatic enzyme, KCl , NaCl , Na_2HPO_4 , $\text{Mg}_2\text{H}_2(\text{PO}_4)_2$, NaHCO_3 , $\text{CaH}_2(\text{CO}_3)_2$, and KCNS . In the dog, the saliva obtained by nerve-excitation differs according to the nerve supply which is irritated: the **chorda tympani**, or **cerebral saliva** contains 12 to 14 p/m of solids; sp. gr. 1004 to 1005.6; is more abundant and contains less mucin than the **sympathetic saliva**, which contains 16 to 28 p/m of solids; sp. gr. 1007.5 to 1018.

The **sublingual saliva** is clear, viscid, alkaline, and contains mucin, a diastatic enzyme and potassium thiocyanate.

The **parotid saliva**, which may be obtained by a canula inserted into Steno's duct, is a thin liquid, usually alkaline, but sometimes neutral, or even faintly acid; sp. gr. 1003 to 1012. It contains 5 to 16 p/m of solids, among which are a small quantity of albumin and a diastatic enzyme, but no mucin. Potassium thiocyanate is sometimes present.

Mixed saliva consists of the above, plus the secretions of the mucous glands. It is colorless, tasteless, odorless, opalescent, frothy, slightly viscid; and cloudy from the presence of epithelium, mucus corpuscles, leptothrix, and food particles. On exposure to air it becomes more cloudy and covered by a pellicle, which consists of calcium carbonate. Its reaction is alkaline, the average alkalinity being equal to 0.8 p/m of Na_2CO_3 , and diminishing, sometimes to acidity, after meals. Sp. gr. 1002 to 1008. It contains 5 to 10 p/m of solids, of which the organic constituents are albumin, mucin, urea, thiocyanate, and two enzymes, **ptyalin** and **maltase**. According to an analysis of Hammerbacher, it has the composition: Water: 994.2; mucus and epithelium: 2.2; soluble organic constituents: 1.4; thiocyanate: 0.04; salts: 2.2. The composition of the ash in 1,000 parts is: K_2O -457.2; Na_2O -95.9; CaO and traces of Fe_2O_3 -50.11; MgO -1.55; SO_3 -63.8; P_2O_5 -188.48; Cl -183.52.

Saliva enzymes.—The saliva contains two enzymes: one amylolytic, converting hydrated starch into maltose and iso-maltose (p. 319), which exists in human saliva at all ages, but not in the saliva of the carnivora, known as **ptyalin**. The other **maltase**, present in the saliva in small amount only, which converts maltose into glucose. Ptyalin has not been obtained in a condition of purity. Gautier's method gives the product most nearly approaching purity: the saliva is treated with a large quantity of strong alcohol; the precipitate is collected and redissolved in water; albumins are precipitated by mercuric chlorid and separated by filtration; the excess of mercury is removed by hydrogen sulfid; the salts are removed by dialysis; and the ptyalin again precipitated by alcohol.

The activity of the amylolytic action of saliva is directly proportionate to the quantity of the enzymes present. The most favorable reaction is a very faintly acid one, due to carbonic acid, and the activity is diminished by either an alkaline reaction or an acid one due to mineral acids. The action is completely arrested by the presence of 0.03 p/m of HCl. The most favorable temperature is 40° (104° F.). The accumulation of its products interferes with the continuance of the action, and it is therefore more rapid and extensive when it takes place in a dialyser than when it occurs in a glass vessel. On the other hand, it is favored by the presence of peptones. The presence of 0.05 p/m of HgCl_2 arrests the action, and a like result is produced by 5 p/m of MgSO_4 , while 0.25 p/m of the latter salt favors the action.

The total quantity of saliva secreted in 24 hours has not been directly determined in the human subject. It is estimated at from 600 to 1,500 cc. During mastication 1 gram of salivary gland produces 13 grams of saliva per hour. The quantity is increased by pilocarpin and by eserine, and diminished by atropine. Many metallic salts are eliminated by the saliva, e. g., those of mercury and potassium, and the bromides and iodides; others do not appear in the saliva, e. g., the salts of iron. The quantity is pathologically increased in poisoning by the soluble mercurials, the mineral acids and alkalies; in neurotic conditions, and in inflammatory diseases of the mouth. It is diminished in febrile diseases, in diabetes, sometimes in nephritis, and under violent psychic emotions. In diabetes the saliva contains sugar in about 54 per cent of the cases examined.

Salivary calculi are rarely met with, varying in size from mere granules to masses weighing 18.6 grams. They consist principally of calcium carbonate, with some tricalcium phosphate, and from 50 to 368 p/m of organic matter.

GASTRIC JUICE AND GASTRIC DIGESTION.

While at rest, in the intervals between digestion, the stomach contains only a thick, slimy, neutral, or even alkaline liquid, the gastric mucus, or *succus pyloricus*, so-called because it is the product of glands located principally at the pyloric end. The true gastric juice is produced only during digestion, or by stimulation of the secreting glands, the fundus, or pepsin glands, by "chemical" or "psychic" action. The gastric juice of man has been obtained free from saliva in one case only, that of a boy of five years having an œsophageal stricture and a gastric fistula (Hornborg). Mixed with saliva, it has been obtained in cases of traumatic (Beaumont), or surgical (Richet) gastrostomy. From animals it may be obtained pure by the establishment of gastric and œsophageal fistulæ.

The gastric juice is a slightly cloudy, almost colorless liquid, sp. gr. 1001 to 1010, having an acid taste and a strongly acid reaction. It deposits a sediment, which, unmixed with food particles, contains gland cells and nuclei, mucus corpuscles and altered cylindrical epithelium.

According to an analysis by Schmidt of human gastric juice, mixed with some saliva, it contains: Water -99.44, solids -0.56, free hydrochloric acid, 0.25. The solids consist of: organic substances (pepsin, etc.) -0.32, NaCl -0.14, KCl -0.05, CaCl_2 -0.006, phosphates of Ca, Mg, and Fe -0.015. Among the organic constituents are a small quantity of a nucleoproteid, a mucin, a thiocyanate and albumose (?), and two or possibly three enzymes, **pepsin**, **pseudopepsin** and, it is claimed by some and denied by others, a saponifying enzyme, a **lipase**.

The chief function of the stomach is to serve as a receptacle in which the food may be stored, and mixed by the action of the muscular coats of the organ, both orifices being closed the while by contraction of the sphincters. In the stomach the proteins are to a considerable extent converted into soluble and absorbable products, but neither for this nor for other use is the stomach an essential organ. The solution of the proteins is accomplished more thoroughly and more rapidly by tryptic digestion in the intestine, which in fact terminates the process begun in the stomach, but not completed therein in the time during which the food remains subject to gastric action. Indeed dogs, after ablation of the stomach, may live for years in perfect nutrition and passing normal fæces, the only departure from the normal in them being that, because of the absence of the receptacle, they take food in smaller quantities and more frequently, and that with time the intestine becomes dilated. Another function of the gastric secretion, claimed by some to be its most important utility, is the destruction of bacteria, taken in with the food and drink, by the germicidal action of the acid.

It is now established that the **free acid** of the normal, unmixed gastric juice is hydrochloric acid. During digestion lactic acid or butyric or acetic acid may be present. They are, however, not products of secretion, but are derived from constituents of the food. The amount of hydrochloric acid present varies in different animals, and, within narrower limits in the same animal at different times. The gastric juice of the dog contains from 2 to 6 p/m, that of the cat about 5 p/m. The proportion usually accepted as present in human gastric juice is 2 to 3 p/m; but in Hornborg's case it was found to vary from 3.65 to 5.66 p/m, the mean of which is 4.66 p/m.

The exact mechanism of the formation of the gastric hydrochloric acid is unknown. That it is derived from the chlorids of the blood

is most probable, although it may result from decomposition of chlorinated amids, which have been found to exist in gland tissues. A fact which supports the supposition of the derivation from the chlorids is that if dogs be given a diet from which chlorids are excluded the hydrochloric acid, after a time, ceases to be formed, while pepsin continues to be secreted; and if now the animal be given bromids, iodids, or chlorids, the gastric juice will contain hydrobromic, hydriodic, or hydrochloric acid, as the case may be. The most probable supposition with regard to the method of formation of the acid from the chlorids is that it is produced by chemical action, the chlorids being decomposed by the free carbon dioxid (or carbonic acid) in the blood, by mass action, according to the equation: $2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{HCl}$; or it may be the result of decomposition of calcium chlorid by the disodic phosphate of the blood: $2\text{Na}_2\text{HPO}_4 + 3\text{CaCl}_2 = \text{Ca}_3(\text{PO}_4)_2 + 2\text{HCl} + 4\text{NaCl}$. The former reaction is the more probable, because of the generation of alkali, mentioned below, during stomach digestion. The reaction: $2\text{NaCl} + \text{CO}_2 + \text{H}_2\text{O} = \text{Na}_2\text{CO}_3 + 2\text{HCl}$ implies the formation of a quantity of alkali equivalent to the amount of acid generated, which should manifest itself somewhere in the system to a degree proportionate to the quantity of acid formed at different times. It is supposed that the alkali thus produced enters into combination with the lecithalbumins which exist in gland cells. Whether this is the case or not, it is known that the acidity of the urine varies inversely with the activity of hydrochloric acid formation; and that the urine may even become alkaline during the greatest activity of stomach digestion and in hyperchlorhydria.

Pepsin and Pepsinogen.—Pepsin exists in the gastric juice of all vertebrates, and at all ages, except that it is not secreted by suckling pigs or puppies. It has not been obtained in a condition of purity, the nearest approach thereto being the product of Peckelharing's method: The gastric juice, collected from dogs having oesophageal and gastric fistulæ, is filtered and dialysed at near 0° for 20 hours. The precipitate formed is collected by the centrifuge and filtration, washed with water and dried over H_2SO_4 . A further portion is obtained by precipitation by half saturation with ammonium sulfate, and removal of salt by dialysis. The united precipitates are dissolved in 0.2 per cent HCl , reprecipitated by dialysis and dried over H_2SO_4 . A less pure product is obtained by Brücke's method: The mucous membrane is extracted with water containing phosphoric acid; the filtered extract is treated with lime water; the precipitate of tricalcic phosphate containing the pepsin, which it carries down mechanically, is dissolved in dilute hydrochloric acid, and the solution freed from salts by dialysis. For digestion experiments an extract

made by macerating the mucous membrane in glycerol containing 1 p/m of HCl and filtered after 8-14 days, may be used. Pepsin is soluble in water and in glycerol, from which it may be precipitated by alcohol. It does not give the albumin reactions. It is precipitated by half saturation with ammonium sulfate. It does not dialyse. In aqueous solution its activity is rapidly destroyed by boiling, more slowly in neutral solution at 55°, in acid solution at 65°, at 70° in presence of peptones, and quite rapidly even at 38-40° in presence of very small quantities of alkaline carbonates. When dry it may be heated to 100° without decomposition. The characteristic property of pepsin is that it dissolves albumins, with formation of albumoses and peptones, in acid, but not in neutral or alkaline solutions.

Pepsinogen, or propepsin, is the zymogen from which pepsin is formed by contact with hydrochloric acid, and is probably produced by the chief cells of the fundus glands. The mucous membrane of the fasting stomach yields to dilute hydrochloric acid an actively digesting extract, even after treatment with 1% sodium carbonate solution, at 40°, which very rapidly destroys the activity of pepsin, but acts only very slowly upon pepsinogen. It has been supposed that pepsinogen and hydrochloric acid combine chemically together to form a definite compound, the active material of the gastric juice, which has been called **pepsohydrochloric acid**.

As has been stated above, the characteristic reaction of pepsin is its power of dissolving albumins in acid solution. If a fragment of coagulated white of egg be immersed in HCl of 2-4 p/m at 40° it is not affected, but if a trace of pepsin be also present, the edges of the fragment are soon rounded, and the material becomes transparent, and finally dissolves. A similar effect is produced more rapidly and at a lower temperature (20°) with fibrin. A similar action, but slower, occurs with acids other than hydrochloric, diluted strong acids acting better than weak acids. Taking the digestive power of pepsin with HCl as 1,000, that with HNO₃, H₂SO₄, lactic, acetic and butyric acids is 932, 909, 603, 396 and 336 respectively. While hydrochloric acid is the most highly dissociated of these acids, the digestive power of the other acids is not proportionate to their electrical conductivity, although that of the organic acids is much lower than that of the mineral acids. The rapidity of the action is also affected by other conditions: it is more rapid if the products of the action be removed by dialysis than if they be allowed to accumulate; and it is less rapid in presence of salicylic acid, metallic salts, alkaloids, phenol, sulfates, or of alcohol in greater proportion than 10 per cent. The most favorable temperature is 40°, and the most advantageous proportion of HCl about 2.5 p/m.

Another enzyme, called **pseudo pepsin**, is secreted at the pyloric

end of the stomach, and probably also at the cardiac end. It differs from pepsin in that it acts not only in an acid liquid but also in one which is faintly alkaline, and in that it produces tryptophane as one of the products of its prolonged action, which pepsin does not do.

The conversion of albumin into peptone is by no means a simple process. The protein, behaving as a base, first enters into combination with the hydrochloric acid, to form an acid albuminate. The amount of acid so combined with the protein is from 5 to 15 per cent of the weight of the latter, the proportion being smaller with the native albumins and greater with their products of hydrolysis, which, it may be assumed, contain a greater number of basic hydroxyls. The acid in combination in acid albuminates and with albumoses is referred to as "loosely combined," or "protein" hydrochloric acid. The acid albumin then undergoes gradual cleavage, producing numerous products of progressively diminishing molecular weight, diminishing proportionate carbon content (because of the addition of water in hydrolysis), and increasing diffusibility as the decomposition advances through the albumoses, until the final products, the peptones, are reached. The formation of acid albuminates as an intermediate stage in the transformation of native or coagulated proteins into albumoses is, however, not essential, and, while acid albuminates do not occur in the stomach in complete absence of albumoses, the latter may be present when no acid albuminate can be detected. This may be due either to the conversion of acid albuminate into albumose immediately upon its formation, or to its non-formation. The latter view is more probably the true one, as the transformation of acid albuminate into albumose does not occur rapidly. It is also claimed that acid albuminates and primary albumoses may be formed together as split products of the parent protein, that, in other words, acid albuminates are parallel products with the primary albumoses.

In the several stages of hydrolytic decomposition it becomes evident that the protein molecule contains two unsymmetrical fractions which behave differently towards proteolytic enzymes and other solvents. One of these readily hydrolyses to soluble products, while the other resists the action of enzymes and acids much more obstinately. The more readily soluble fraction is designated as the **hemi group**, the more resistant as the **anti group**. On decomposition the anti compounds yield larger quantities of diamido acids than do those of the hemi group.

Intermediate between the acid albuminates and the peptones a series of substances, called **albumoses** or **propeptones**, are formed. From the different proteins different albumoses are derived. The **proteoses** are derived from the true albumins and from the albumin components of the proteids; the **gelatinoses**, **keratinoses**, etc., from

the albuminoids. It is also highly probable that each species of albumin furnishes an individual series of proteose. These are designated as **globulinoses**, **vitellinoses**, **fibrinoses**, **caseinoses**, etc., according to their origin.

All albumoses, except heteroalbumose, are soluble in water, all are soluble in hydrochloric acid as chlorids, whose solutions are highly dissociated. They are precipitated by potassium ferrocyanid and acetic acid, by nitric acid either in watery solution or in solutions saturated with sodium chlorid, and by phosphotungstic acid and other alkaloid reagents, the precipitates in all cases being dissolved by heat and reappearing on cooling. They all give the xanthoproteic and Adamkiewicz reactions, and a red color with the biuret reaction, except protoalbumose, which gives a violet. The best studied of the albumoses are the fibrinoses, which are conveniently obtained from "Witte's peptone," a product of artificial peptic digestion of fibrin, which contains very little true peptone, and consists chiefly of fibrinoses with some mucinoses.

The first dissolved products derived from the acid albumins, or formed directly from the albumins, are known as **primary albumoses**. They are of three kinds: **protoalbumose**, derived from the hemi group, and **heteroalbumose** and **glucoalbumose** from the anti group. The heteroalbumoses are the albumoses most nearly related to the native albumins. Besides these albumoses there is produced at this stage an insoluble residue of **antialbumid**, which is difficultly soluble, even by tryptic digestion. Glucoalbumose differs from the other primary albumoses in the important respects that it contains a carbohydrate component and therefore responds to the Molisch reaction, which the others do not, and that it is not salted out from neutral solution by one-half saturation with ammonium sulfate, but only by complete saturation with that salt. It is, however, classed as a primary albumose, being a direct derivative of the acid albumin or native albumin. Heteroalbumose and protoalbumose differ from the succeeding products, the secondary albumoses, principally in being less diffusible, and in their behavior towards nitric acid, and towards ammonium sulfate. Nitric acid in the cold precipitates these primary albumoses from simple aqueous solution, but the secondary albumoses only in the presence of salts, if at all. Ammonium sulfate precipitates these primary albumoses completely when added to half saturation, but the secondary albumoses are only precipitated by greater concentration of the salt, up to saturation in some cases. Both heteroalbumoses and protoalbumoses are salted out by sodium chlorid, the former from neutral solution, the latter only in presence of acid. The limits of each with ammonium sulfate are 2.6 and 4.4 in neutral solution and 1.2 and 4.3 in acid solution. They form precipitates with

cupric sulfate or acetate, and with protamins and histons. They contain no carbohydrate component.

Heteroalbumose (from fibrin) is very sparingly soluble in water, easily soluble in hydrochloric acid, and partly precipitable from this solution by dilution; soluble in alkalies; and does not dialyse from neutral solutions, and only very slightly from those which are alkaline. It is partly coagulated at 55°–60° in presence of small quantities of salts. The coagulum is soluble by increased heat, and in its own form in dilute hydrochloric acid or caustic soda; it is not denaturized. It is salted out completely from acid solutions by half saturation with sodium chlorid. It is precipitated by alcohol at a concentration of 32 per cent alcohol, a property which is utilized for its separation from protoalbumose, which is still soluble in alcohol of 80 per cent. On decomposition it yields 6.45 per cent of its nitrogen as ammonia, 57.40 per cent as monamido nitrogen, and 38.93 per cent as diamido nitrogen. Among its decomposition products are leucin and glycocoll in large amount, but only traces of tyrosin, and no indole or skatole. It, however, contains an aromatic complex, probably phenylalanin. On further peptic or tryptic digestion it produces deuteroalbumoses A and B and traces of C, and peptone B.

Protoalbumose (from fibrin) is very easily soluble in water, and dialyses more than heteroalbumose. It is only salted out by sodium chlorid on complete saturation in acid solution. It is soluble in 80 per cent alcohol. It is not coagulated by heat. The precipitates which it forms with tannin and other alkaloid reagents are soluble in excess of the precipitant. On decomposition it yields 7.14 per cent of its nitrogen as ammonia, 68.17 per cent as monamido nitrogen, and 24.42 per cent as diamido nitrogen. Among its decomposition products are little leucin, no glycocoll, but much tyrosin, tryptophane, indole and skatole. On further peptic or tryptic digestion it produces much deuteroalbumose A and peptone B, but no deuteroalbumose C or peptone A.

Glucalbumose, also known as *deuteroalbumose Ba*, *deuteroalbumose BII*, and *synalbumose*, is not precipitated from neutral solution, along with the other primary albumoses, by 50 per cent saturation with ammonium sulfate, but only by complete (95 per cent) saturation, along with some of the secondary albumoses, in deuterofraction B (below), from which it is separable by alcohol, which first precipitates out deuteroalbumose BI at 35 per cent, and then glucalbumose at 60–70 per cent, leaving the other deuteroalbumoses in solution. It is the only albumose containing a carbohydrate component, and the sole precursor of peptone A. It not only gives a brilliant Molisch reaction, but an osazone, f. p. 182°–185°, has been obtained from it. It contains but little loosely combined sulfur.

An albumose obtained from Witte's peptone, known as **deuteroalbumose A α** , is also probably a primary product. It is precipitated from neutral solution by sodium chlorid and by copper salts. Its limits with ammonium sulfate are 4 and 5.6.

The primary albumoses on further peptic digestion yield **secondary albumoses**, also called **deuteroalbumoses**, which are soluble in water and diffuse more than the primary albumoses, but less than the peptones. They give the xanthoproteic and biuret reactions and, except deuteroalbumose C, the Millon reaction. Excepting glucoalbumose, they contain no carbohydrate component and therefore do not give the Molisch reaction. They are not precipitated by copper salts. They are only precipitated by nitric acid in presence of salts, if at all. They are not salted out by 50 per cent saturation with ammonium sulfate in neutral solution, but on increasing the concentration, and finally acidulating, they are divided into three "fractions," which are themselves mixtures, except probably the last.

Deutero fraction A, derived chiefly from the hemi group, but also from the anti group, is precipitated from neutral solution by 62 per cent saturation with ammonium sulfate. Its limits with this salt are 5.4 and 6.2 in neutral solution, and 4.7 and 5.9 in acid solution. On treatment with 70 per cent alcohol this fraction is divided into two parts: **deuteroalbumose A**, which goes into solution, and **thioalbumose**, which remains insoluble. The former contains 0.8 per cent sulfur, and the latter 2.97 per cent, of which the major part is in the loosely combined condition.

Deutero fraction B, derived almost entirely from the anti group, but also from the hemi group, is precipitated from neutral solution by 95 per cent saturation with ammonium sulfate. Its limits with that salt are 7.2 and 9.5 in neutral solution, and 6.3 and 7.7 in acid solution. By alcohol this fraction is divided into three parts. One, **deuteroalbumose B I**, insoluble in 35 per cent alcohol, constitutes the major part of the secondary albumoses from fibrin. It contains no loosely combined sulfur. The second part is **glucoalbumose**, or **deuteroalbumose B II**, which is precipitated by alcohol at 60-70 per cent. The third part, which is still soluble in alcohol at 80-90 per cent, is itself a mixture containing two albumoses, **deuteroalbumose B III α** , **deuteroalbumose B III β** , both of which give the xanthoproteic, biuret and Millon reactions, but not the Molisch, and a melanoidin-like substance, **peptomelanin**, which gives none of these reactions.

Deuteroalbumose C, derived in small quantity and entirely from the anti group in the case of fibrin, is only precipitated by ammonium sulfate at complete saturation and acidulation with sulfuric acid saturated with that salt. It is soluble in 60-70 per cent alcohol. It appears to contain no sulfur. It gives the xanthoproteic and biuret reactions,

but not the Molisch. It yields neither indole nor skatole on decomposition. It produces no peptone, and appears to be intermediate between those substances and the other albumoses in constitution.

The formation of albumoses in peptic digestion at the body temperature begins quite soon. With serum albumin primary albumoses and acid albuminates begin to be formed in less than nine minutes, and in 26 minutes with egg albumin the solution contains not only hetero- and protoalbumose, but also deutoalbumose B. In this early stage, and during the formation of primary albumoses, other products are split off, in small quantity at first, but increasing to a proportion which subsequently remains constant, which are much simpler in constitution than the albumoses. These products, which are formed more abundantly towards the final stages of prolonged peptic and tryptic digestion, are called **peptoids** (p. 617).

In the period during which the food remains in the stomach, usually about four hours, the secondary and even the primary albumoses formed are to some extent absorbed, although their absorption is much more difficult than that of the peptones. In this time peptic digestion proceeds only to the formation of secondary albumoses and peptoids. Peptones are either not formed or are only produced in very small amount. But by prolonged peptic digestion at the body temperature *in vitro* not only are peptones produced, but the decomposition proceeds still further, and the final products are qualitatively the same as those formed by the more energetic tryptic digestion, except that tryptophane is not produced.

The name **peptone** is now applied to all products of decomposition of proteins which cannot be salted out, either from acid, neutral or alkaline reaction, by ammonium sulfate or other salts, and which give the biuret reaction, whatever may be their chemical nature. Among them are compounds which are extremely soluble in water, hygroscopic, crystallizable, highly diffusible, are not precipitated by nitric acid even from solutions saturated with salts, nor by the usual precipitants of the albumins except phosphotungstic and phosphomolybdic acids, mercuric chlorid, tannin, picric acid and alcohol. With the biuret reaction they give a distinct red color.

The mixture of peptones resulting from peptic digestion was formerly considered as an individual substance, known as Kuehne's **amphopeptone**, from its origin from both hemi and anti groups. The deutoalbumoses A and B from fibrin yield peptones, deutoalbumose C does not. The product from deutoalbumoses A, BI, and BIII, undoubtedly a mixture, is known as **peptone B**. It is soluble in 96 per cent alcohol, gives the Millon reaction, is not precipitated by iodopotassium iodid solution in saturated ammonium sulfate solution, and contains no carbohydrate component, and therefore does not give

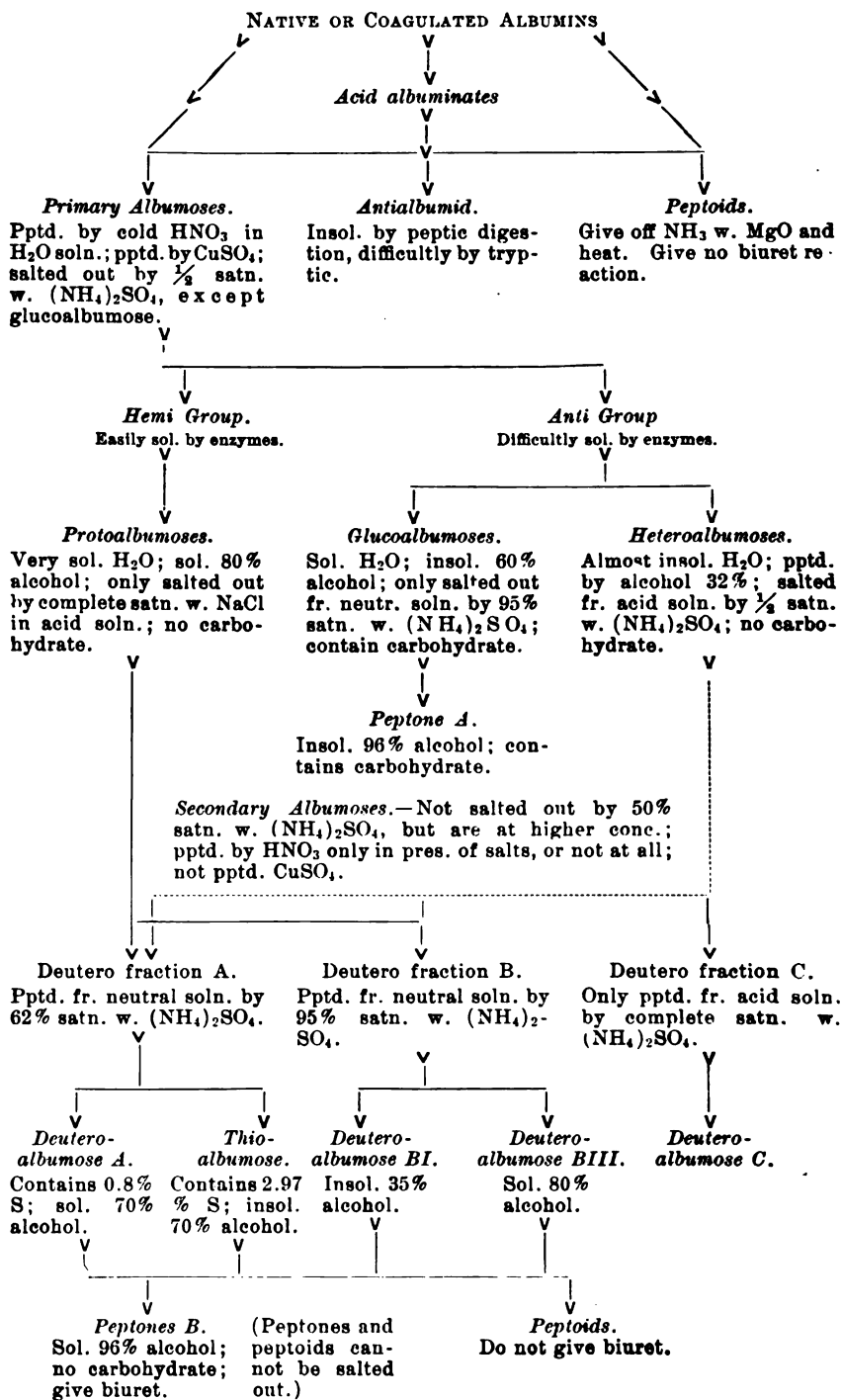
the Molisch reaction. Peptone A, derived from gluealbumose (deuteroalbumose BII), is insoluble in 96 per cent alcohol, is precipitated by the iodopotassic solution, contains a carbohydrate component, and gives a brilliant Molisch reaction.

Probably the only peptones which have been obtained as chemical individuals are the fibrin and glutin peptones of Siegfried. The **pepsin-fibrin-peptones**, α , $C_{21}H_{34}N_6O_9$, and β , $C_{21}H_{36}N_6O_{10}$, are acids, capable of expelling CO_2 from carbonates to form salts, exert constant laevorotation, and give both biuret and Millon reactions. The β peptone can yield the α compound by loss of water. They are amphopeptones in the meaning of Kuehne in that on tryptic digestion they yield anti-peptones (p. 629).

The **peptoids** give off ammonia when heated with magnesia, and are the near precursors of the end products of tryptic and prolonged peptic digestion. They are distinguished from the peptones by not giving the biuret reaction. The polypeptids (p. 415), which still give the biuret reaction, are probably intermediate products between deuteroalbumoses and peptoids. Arginin (p. 418), and **albumin**, a dihexoseamin, $C_{12}H_{24}N_2O_3$, are among the decomposition products of the peptoids. By still longer continued peptic digestion the following end products have been obtained: amidovalerianic acid, leucin, glutamic and aspartic acids, lysin, cystin, putrescin, cadaverin, tyrosin, phenylalanin, oxyphenylethylamin, and skatosin.

The changes above described may be expressed for the fibrinoses in the tabular form of the scheme on p. 618.

Peptic digestion exerts the following actions upon substances other than the native albumins: Milk is "curdled" by the gastric juice, a change which consists in the separation of the "curd" (cheese) and "whey." The former is derived from the nucleoalbumin **casein**, which exists in the milk as its soluble neutral tricalcic salt. This effect has been ascribed to the action of an enzyme, called **chymosin**, or **rennin**, derived from a proenzym, **chymosinogen**, supposed to be secreted by the fundus glands. Chymosin has, however, not been obtained free from pepsin, and the two enzymes are in all likelihood one and the same. The curdling of milk is merely the first stage in the digestion of casein, attended, in the case of this particular protein, by the separation of a temporarily insoluble product. The calcium casein is split into a small quantity of an albumose-like protein, called **whey-albumin**, and a soluble **calcium paracasein**, which latter, combining with soluble calcium salts, produces the curd, insoluble in liquids of nearly neutral reaction. The paracasein so formed is itself a nucleo-albumin, and is split by further peptic digestion into its paranuclein, which remains insoluble, and its albumin component which is then converted into primary and secondary albumoses, etc.,



in the same manner as the native albumins. The **proteids** are split in like manner, their albumin components suffering the same changes as the native albumins. The **nucleins** derived from the nucleoproteids are not acted upon by peptic digestion. Of the **albuminoids** only collagen (or its derivative, gelatin) and elastin are acted upon by the gastric juice, and upon them its action is slow. They are converted into proto- and deuterogelatoses and elastoses, but they yield no hetero product, which offers an explanation for the fact that these albuminoids cannot completely supply the place of native albumins in the dietary. Animal cell membranes and connective tissues, being made up of keratins and elastin or collagen in varying proportions, are acted upon according to their tenure in these constituents. The connective tissue of the panniculus is in great part dissolved, and the fat liberated. Whether or no the stomach produces a lipase, or gastrosteapsin, which saponifies fats, is a mooted question. The diastatic action of the salivary ptyalin continues in the stomach, particularly in the interior of difficultly permeable masses of starchy food, until the acidity of the gastric juice has overcome the alkalinity of the material acted upon. How soon this occurs is not definitely known, but it certainly does not occur immediately, and some time, probably from twenty minutes to half an hour, is required for the secretion of a sufficient amount of acid to cause its presence uncombined. As soon as the reaction becomes acid the amylolytic action ceases.

The duration of stomach digestion differs in different animals. In the herbivora, particularly the ruminants, the stomach is never empty, except after prolonged starvation, while in the carnivora the organ may be completely emptied in two hours after a meal. In man the average period of stomach digestion is from four to six hours. From the stomach the **chyme**, the semi-pasty, acid product of salivary and peptic action upon the food, passes to the duodenum.

The observed **abnormal variations** in composition of the gastric juice relate principally to the free acid. Free hydrochloric acid may be absent (anachlorhydria) in neurasthenic conditions, in chronic gastritis, in carcinoma of the stomach, and in the secondary stage of corrosion by mineral acids or alkalies. It may be present in subnormal quantity (hypochlorhydria) in subacute or chronic gastritis, ulcer of the stomach, dilatation, and the earlier stages of carcinoma. Or the amount may be greater than the normal (hyperchlorhydria) in neurasthenic patients, or, sometimes, in carcinoma. When the amount of free hydrochloric acid is subnormal, fermentative changes, usually prevented by the antifermentative and antiseptic action of the pepsohydrochloric acid, are set up, with the formation of lactic and even of acetic and butyric acids, with liberation of hydrogen and consequent eructations of gas and heartburn. These organic acids

may also frequently be present in the stomach, having been introduced with the food; lactic acid exists in sour-kraut, in pickles, and in all kinds of bread; acetic acid is the acid of vinegar; and free butyric acid may be present in butter. It appears to have been demonstrated that in most cases of carcinoma of the stomach lactic acid is present in the stomach contents in greater amount than can be accounted for by the test-meals which have been used. Pepsin is very rarely absent, only after complete destruction of the pepsin glands by the action of corrosives. Abnormal constituents, not introduced by the mouth, may also be present: urea and ammonium carbonate in uræmia, acetone in acetonuria, the constituents of the blood, or hæmatin, as the result of hemorrhage into the stomach, and, frequently, the constituents of the bile, by regurgitation; also arsenic and morphin when they have been taken in poisonous dose by channels of absorption other than the mouth.

Examination of Stomach Contents.—Usually it is desirable to obtain the gastric secretion as free as possible from the constituents of food articles. With this object the stomach contents are collected after the stomach has been washed out, and the secretion of gastric juice stimulated by a "test-meal." Many such have been recommended, of which probably the most serviceable is that of Boas, consisting of a tablespoonful of rolled oats and a quart of water, boiled down to a pint, to which a little salt may be added. The stomach contents are collected one hour after the meal has been taken.

Total Acidity.—Four factors may contribute to the acid reaction of the gastric contents: free hydrochloric acid, hydrochloric acid in protein combination (see below), organic acids, and acid salts. The sum of these, or of such of them as may be present, constitute the total acidity. This is determined by titrating 5 or 10 cc. of the unfiltered gastric contents with N/10 (one-tenth normal) caustic soda solution, using phenol phthaleïn as an indicator. As each cc. of the N/10 alkali corresponds to 0.00365 gm. of HCl, the number of cc. of alkali used, multiplied by 0.0365 (if 10 cc. of gastric contents have been used) gives the percentage of total acidity, expressed in terms of hydrochloric acid.* Another form of expression is sometimes used, i. e., the number of cc. of N/10 caustic soda solution required to neutralize 100 cc. of the material. This is obtained, if 10 cc. of material are used, by multiplying the number of cc. of N/10 alkali required to neutralize, by 10. The normal total acidity after a Boas meal is 0.15 to 0.30% HCl, which is equivalent to 40 to 80 cc. N/10 NaHO.

Presence of Free Acids.—The next step is to determine whether any of the total acidity is due to free acids, and if it is to what acid or acids. This is accomplished by the use of indicators, sub-

stances giving different colors with certain classes of acid or alkaline substances. The red color of alkaline phenolphthaleïn, used as an indicator above, is discharged by all four factors contributing to the acidity of the gastric contents, therefore it is used in determining the total acidity. Congo red forms an orange-yellow solution in alcohol, which, when largely diluted, is turned blue by a drop or two of a .001 per cent solution of HCl, or by other free mineral acids, or by organic acids if present in sufficient quantity, but not by acid salts. If, therefore a few drops of the gastric contents give a blue color with a drop or two of dilute congo-red solution, a free acid is present.

To detect free hydrochloric acid an indicator must be used which will react with mineral acids, but not with organic acids or with acid salts. Several have been suggested, of which the following are desirable: (1) *The phloroglucin-vanillin reaction*—Phloroglucin and vanillin are dissolved in alcohol in the proportion of 2 gm. of the former and 1 gm. of the latter in 100 cc. of the solvent (Gunzburg's reagent). A few drops of the filtered gastric contents and the same quantity of the freshly-prepared reagent are mixed in a porcelain dish, and evaporated on the water bath: in the presence of free mineral acids a brilliant scarlet color is produced, beginning at the upper border. Delicacy=.05 p/m HCl. Not interfered with by albumoses or peptones. (2) *Resorcin-sugar*—The reagent (Boas' reagent) is made by dissolving 5 gm. of resorcinol and 3 gm. of sugar in 100 cc. of dilute alcohol, and is used in the same manner as the phloroglucin-vanillin reagent, giving a rose-red color with free mineral acids. Delicacy=.05 p/m HCl. (3) *Dimethyl-amido-azobenzene*—(Töpfer's test) forms a yellow alcoholic solution, which turns red with free mineral acids. Delicacy=.02 p/m HCl. This and other similar tests are applied by simply mixing a few drops of the indicator with a like quantity of the contents. Papers colored with the several indicators are sometimes used, but they are not as delicate as the solutions.

Negative results of these tests with a sample of gastric contents of *unknown origin* do not prove that the stomach is not secreting the normal quantity of hydrochloric acid (see Quantitative, below). Such samples are met with to which double the amount of HCl normally present may be added, and not reveal its presence upon application of the tests.

Quantitative Determination of HCl.—Chlorin may exist in the gastric contents during digestion of usual food articles in three forms of combination: as free hydrochloric acid, as "loosely combined" acid, and as chlorids, all of which must be taken into consideration, along with the acid salts and organic acids, in determining the amount of HCl produced by the stomach. By "loosely combined

HCl" is meant that portion of the free HCl secreted by the stomach which has entered into combination with the proteins to form acid-albumins; and the "effective HCl" is, clearly, the sum of the free and the loosely combined. The quantity of acid that can be thus combined is considerable. Thus 100 gm. of each of the following food articles can take up the amounts of HCl stated, in grams: Cheese -1.3 to 2.6, meat -1.6 to 2.2, milk -0.42, bread -0.3 to 0.7, beer -0.15.

Of the several methods which have been devised, probably the most desirable are those of Töpfer and of Martius and Lüttke, somewhat modified, the former, based upon the use of indicators, being the more rapid of the two, the latter, based upon chlorin determinations in part, the more accurate.

Töpfer's Method.—Three samples of 10 cc. each are separately titrated with N/10 NaHO solution; in (1) using phenolphthalein as an indicator, and carrying the addition of alkali to a distinct red, not to faint pink as is usual. This gives the total acidity (A), made up of free HCl (L), protein HCl (C), and organic acids and salts (O). In (2) alizarin is used as an indicator, to pure violet. This gives the acidity due to (L+O), and, therefore the result of (2), subtracted from that of (1), leaves the value of (C)=protein HCl. In the third sample (3) dimethyl-amido-azobenzene is used as an indicator, to yellow. This gives the value of (L) alone, i. e., free hydrochloric acid. If the value of (O) be desired, it may be obtained by subtracting the result of (3) from that of (2). In each of the above titrations the number of cc. of alkaline solution used, multiplied by 0.0365, gives the result, expressed in percentage of HCl.

Martius and Lüttke's Method.—Four samples of 10 cc. each of the filtered material are taken. In (1), the total chlorin (T) is determined either volumetrically with a N/10 solution of AgNO₃ and thiocyanate as an indicator, or, preferably, gravimetrically, by the usual methods. The result, expressed in terms of HCl=(T), consists of free HCl (L), protein HCl (C), and chlorin in chlorids (F). In the second 10 cc. (2), the chlorids (F) are determined by evaporating to dryness, incinerating at dull redness, redissolving in water, and determination of HCl as in (1). The effective HCl (L+C) is determined by subtracting (F) from (T). In the third sample (3), the total acidity (A) is determined by titration with N/10 NaHO solution and phenolphthalein. The acidity due to organic acids (O) is arrived at by subtracting (L+C) from (A). In the fourth sample (4) the free HCl (L) is directly determined by titration with N/10 NaHO, using dimethyl-amido-azobenzene as the indicator. Finally, the value of (C) is obtained by subtracting (L) from (L+C).

Mörner and Sjöqvist's Method.—By this method the quantity of

"effective HCl" can be determined more expeditiously than by Martius and Lüttke's method, and as accurately. It is based upon the fact that if the gastric juice be evaporated with BaCO_3 , and the residue incinerated, both free and protein hydrochloric acid form BaCl_2 , while the organic acids are destroyed, and neither the acid salts nor the chlorids enter into consideration. Pure, pulverized BaCO_3 is added to 10 cc. of the gastric contents, and evaporated to dryness. The residue is moderately ignited until white, and extracted with hot water. To the filtered extract (about 50 cc.) an equal volume of 94 per cent alcohol and 0.75 cc. of a 10 per cent solution of sodium acetate in dilute acetic acid are added, and the barium determined by titration with a solution of potassium dichromate containing 8.5 gm. p/L, standardized with a N/10 solution of BaCl_2 , and using paper impregnated with tetramethyldiamidobenzene as an indicator, the end reaction being the formation of a blue color in one minute. If the $\text{K}_2\text{Cr}_2\text{O}_7$ solution and the N/10 BaCl_2 solutions are equivalent, the amount of hydrochloric acid is obtained by multiplying the number of cc. used by 0.00405.

Lactic Acid.—The presence of lactic acid is detected by: (1) *Ufflemann's reagent*, which consists of a solution of Fe_2Cl_6 and phenol diluted to an amethyst-blue color, which is changed to yellow by lactic acid. In order to avoid error by the action of other substances which have a like action upon the reagent, 10 cc. of the filtered gastric contents are agitated with ether, and the ethereal extract separated and agitated with the reagent; or it may be evaporated, the residue dissolved in water, and the solution added to the reagent. (2) *Boas' method*, which is more reliable, and which depends upon the formation of aldehyde from lactic acid by the action of oxidants (p. 341), and the behavior of aldehyde with Nessler's solution (p. 151). Ten cc. of the contents are treated with excess of BaCO_3 , and evaporated to dryness on the water bath, to a syrup; this is treated with dilute H_3PO_4 , heated to boiling, cooled, and extracted with ether by agitation. The separated ethereal extract is evaporated and the residue extracted with water. The aqueous solution is then mixed with 5 cc. H_2SO_4 and a little MnO_2 , and distilled, the distillate being received in a cylinder containing Nessler's reagent, which is turned yellow, or deposits a yellow-red precipitate, if aldehyde be present. Or the distillate may be received in a N/10 normal solution of iodine, with which aldehyde forms iodoform, recognizable by its odor, or by the formation of a yellow, crystalline precipitate, if the quantity be sufficient.

The iodine reaction is utilized for quantitative determination. The distillation with H_2SO_4 and MnO_2 is conducted in a current of air, and continued until four-fifths of the material have distilled over. The dis-

tillate is heated with 20 cc. normal KHO solution and 20 cc. N/10 iodine solution, agitated and allowed to stand a few minutes. The amount of unused iodine remaining is then determined by addition of 20 cc. HCl, sp. gr. 1.018, and titration with N/10 sodium thiosulfate solution, using starch paste, added near the end of the titration, as an indicator. The number of cc. of iodine solution used in the formation of iodoform, multiplied by 0.003388, gives the quantity of lactic acid.

The presence of butyric acid may be recognized by extracting 10 cc. with 50 cc. of ether by agitation, evaporating spontaneously, and adding a few drops of water and some solid CaCl_2 to the solution, when oily drops separate, and the characteristic odor of butyric acid is developed. The quantity of volatile acids, butyric and acetic, may be ascertained by determining the total acidity in one sample of 10 cc. by the method given above; evaporating another sample of 10 cc. to a syrup, redissolving in water, and determining the acidity of the solution. The difference between the two determinations is the acidity due to volatile acids.

Pepsin and Pepsinogen.—If free HCl be present the gastric contents are examined for the presence of pepsin by placing about .05 gm. of coagulated white of egg, cut into discs or cubes, in 25 cc. of the material, which is then kept at 38-40°. Digestion should be complete in about three hours, or the edges of the fragments rounded perceptibly in less time. If no free HCl be present, pepsinogen is tested for as above, five drops of dilute HCl having been added to the material. Should the result be negative, 200 cc. of N/10 HCl should be introduced into the stomach, the contents of which are removed in half an hour and tested as above.

No quantitative method of determining pepsin is possible at present. Comparisons of the degrees of activity of a given sample of gastric contents with some pharmaceutical pepsin may be made by adding 5 cc. of the former and 0.5 gm. of the latter in two tubes to 10 cc. of a 1% solution of serum albumin containing 3 p/m of HCl, and after 24 hours determining the amount of albumin remaining undigested, by the usual methods (p. 738).

Sometimes it is desirable to test the stomach contents for the **products of digestion**. This is done as follows: The filtered contents are accurately neutralized with dilute NaHO, using litmus as an indicator; if **syntonin** be present, it will form a precipitate, soluble in excess of acid or of alkali. The liquid, freed from syntonin, is acidulated with very dilute acetic acid, and an equal volume of saturated NaCl solution is added, and the mixture heated to boiling; a coagulation indicates the presence of **native albumins**. A part of the filtrate is tested for **primary albumoses** by addition of HNO_3 and

heating; a precipitate in the cold, which disappears with heat, and returns on cooling, indicates their presence. Another portion of the filtrate is tested for **secondary albumoses**, which are precipitated, if not present in too small amount, by saturation with NaCl. The remainder of the filtrate is saturated with $(\text{NH}_4)_2\text{SO}_4$, filtered, treated with concentrated NaHO solution in slight excess, allowed to settle, decanted, and the clear liquid tested for **peptones** with a few drops of a 2% CuSO_4 solution, which gives a rose-red or reddish-violet color in the alkaline solution if they are present.

Ewald's test for the activity of the **motor function** of the stomach depends upon the fact that salol passes through the stomach unchanged, but is decomposed in the intestine, with liberation of salicylic acid, whose presence in the urine may be then detected. About 0.7 gm. of salol are administered by the mouth, and the urine is collected at regular intervals, and tested by addition of a few drops of Fe_2Cl_6 solution, which gives a violet color with salicylic acid. The reaction should appear in 40 to 70 minutes, and should cease in 30 hours. The **resorptive activity** of the stomach may be tested by administering 0.2 gm. of potassium iodid in a capsule, and testing the saliva every two minutes by moistening a test-paper, made by impregnating filter-paper with starch paste, with the saliva, and then touching it with a glass rod dipped in yellow HNO_3 , which turns blue with KI. The reaction should be obtained in 5-10 minutes.

PANCREATIC SECRETION AND DIGESTION.

The digestive action of the salivary secretion is limited in duration and in character, that of the gastric juice may be dispensed with, and the functions of both are continued and may be completely replaced by those of the pancreatic secretion. The pancreatic juice may therefore be said to be the most active and essential agent of digestion. The pancreas, or a corresponding organ in which certain of the functions of the liver are associated with its own, exists in all animals, and is necessary to life. The pancreas also plays a part in the essential metabolic processes of the system, and its removal is followed by the appearance of an intense glycosuria, attended by acidosis, i. e., the increased formation of acetone and related acid substances.

The digestive function of the pancreas only will be considered in this place. The pancreatic juice is produced continuously in the herbivora, but intermittently in the carnivora, while in both its formation ceases during starvation. In the carnivora the maximum of secretion is reached (with milk feeding) in about three hours after eating, with another rise, following a diminution, from two to four hours later. Its secretion follows the passage of the acid chyme into

the duodenum. The activity of the pancreatic cells is probably incited in two ways. Partly by reflex nervous stimulation (Pawlow). This is, however, not the only method, as injection of an acid into a loop of jejunum whose nerve supply has been completely severed still provokes activity of the gland. The second, and probably the most important, method of stimulation is the production in the upper intestine of a substance, called **secretin**, which, being carried by the blood to the pancreas, stimulates its cells to secretion (Baylies & Starling). The epithelial cells of the duodenum and upper jejunum produce a **prosecretin**, which on contact with acids forms secretin. This is supposed to be a definite chemical entity. It is not an enzyme, because it may be boiled in acid, neutral or alkaline solution without suffering harm, and it is not precipitated either by tannin or by alcohol. Its injection into the circulation is followed by increased secretion of normal pancreatic juice, and also of bile. Moreover, if an acid be injected into the duodenum of one dog, pancreatic secretion is stimulated in a second dog into whose veins the blood of the first is transfused. Neither secretin nor prosecretin is identical with enterokinase (p. 627).

The secretion has been obtained from man in rare cases of pancreatic fistulæ following surgical operations. It can be obtained from temporary fistulæ, established in the pancreatic duct in animals, or from permanent fistulæ, but the secretion obtained from the latter becomes changed from the normal in composition in a few hours. In dogs the amount normally secreted is estimated at from 2.5 to 5 gms. per kilo per diem, but the amounts obtained from permanent fistulæ are much greater. The quantity secreted by man has been calculated to be 150 gms. daily, although in two cases of pancreatic fistulæ, in which, however, the secretion was probably modified as is that of permanent fistulæ in animals, the amounts obtained were 600 gms. (Pfaff), and 700 to 900 gms. (Glæssner), respectively. The pancreatic juice of the dog is clear, transparent, colorless, odorless, viscid, sp. gr. 1008 to 1010, and strongly alkaline, the alkalinity being equal to about 3 p/m of Na_2CO_3 . The alkalinity and trypsin content of this secretion increase during digestion. On exposure to air it rapidly loses its transparency and its viscosity, deposits leucin and tyrosin crystals, and its proteins undergo putrefactive changes, to which, as well as to autolysis, it is exceedingly prone.

Composition.—The secretion from a temporary fistula in the dog contains: water, 900.8; solids, 99.2. The solids consist of mineral substances 8.8, and organic substances, 90.4, of which 60.2 are proteins and enzymes (Schmidt). In the secretion from a permanent fistula in the dog the amount of solids is notably less: water, 980.44; solids, 19.60, of which 3.57 mineral salts, and 16.03 organic (Krüger). In another dog with a temporary fistula the solids were found to vary

with the quantity of the secretion from 20 to 93 p/m (Lesage). The pancreatic secretion found in an occluded canal of Wirsung, in a man suffering from cancer, contained 24.1 p/m of solids, of which 11.5 p/m consisted of proteins and enzymes, and 6.2 of salts (Herter). The secretion from a pancreatic fistula remaining in a woman after extirpation of a carcinoma contained 135.9 p/m of solids, of which 3.44 were mineral salts and 92.05 proteins (Zawadsky). The quantitative composition is therefore subject to great variations.

The mineral constituents are sodium and potassium chlorids and phosphates, sodium and potassium carbonates, to which the liquid owes its alkalinity, and compounds of calcium, magnesium and iron. The organic constituents include small quantities of leucin, tyrosin, purin bases, fat, soaps, fibrinogen, a nucleoproteid, much albumin and globulin, sufficient to cause the liquid to form a solid coagulum when heated after acidulation, and at least three enzymes or their zymogens, one a proteolytic enzym, **trypsin**, another an amylolytic enzyme, **pancreatic diastase**, or **amylopsin**, and the third, having a saponifying action, **steapsin**.

Trypsin.—This and other pancreatic enzymes do not exist as such in the gland cells. These, as well as the pancreatic secretion as collected from the duct, contain the zymogen, and neither the secretion nor an extract of the fresh pancreas has any proteolytic action. Trypsin is produced from trypsinogen by exposure of the hashed pancreas to air. In the body, the formation of trypsin from trypsinogen is due solely to the action of another enzyme, **enterokinase**, produced in the intestinal mucous membrane. Neither the acid of the gastric juice nor other acids produce this effect, as was formerly supposed, but, on the contrary, they tend to hinder the action of enterokinase. Trypsinogen is not formed during fasting, but its production begins soon after food is taken, and reaches its maximum in about four hours. Trypsin is very soluble in water; insoluble in alcohol. In the purer states in which it may be obtained it is insoluble in glycerol, although in a more impure form it is soluble in that liquid, which may be used to extract it from the hashed gland. In acid solution trypsin is destroyed at 45°, less rapidly in the presence of albumoses, and in alkaline solution (0.25–0.5 per cent NaHO) at 50°. When dry it is not affected by a temperature of 100°, and at higher temperatures it is gradually destroyed, completely at 160°. In aqueous solution crude trypsin is decomposed into an albumin, which coagulates, and an albumose by addition of a little acid and boiling. But trypsin has been obtained which does not give the biuret reaction, and therefore cannot contain an albumin.

Trypsin is obtained in a condition most nearly approaching purity by the Kühne-Gautier method: The hashed pancreas, after a day's

exposure to air at the room temperature, is extracted in the cold with 1 p/m aqueous salicylic acid. The extract is rendered faintly alkaline with thymolized Na_2CO_3 solution (5 p/m), and autolysed for a week at 38° to remove albumins and the other enzymes as much as possible. The filtered solution is then saturated with ammonium sulfate; the precipitate, which contains the trypsin, washed with saturated ammonium sulfate solution, dissolved in water, subjected to dialysis, and precipitated with alcohol.

Action of Trypsin.—The most characteristic property of trypsin is its power of dissolving native or coagulated albumins in alkaline or extremely faintly acid reaction, with formation of albumoses, peptones and simpler crystalline products. Normally it continues and supplements the similar action of pepsin, but such preliminary treatment of the proteins is by no means necessary to its efficiency. Not only is it capable of digesting native albumins, but its action in this regard is more rapid than that of pepsin, and, in equal time, proceeds to more advanced decomposition. If putrefaction be prevented, the pancreas rapidly undergoes autolysis at 38° , resulting in the decomposition not only of the proteins of the organ, but also of the other enzymes and zymogens. The action of trypsin upon fibrin is the most energetic, but it also dissolves albumins and globulins, native or coagulated, rapidly, and gelatin, which is only slightly acted upon by pepsin, as well. It acts best in the presence of 3 to 4 p/m of Na_2CO_3 . Its action is arrested by the presence of even very small quantities of mineral acids, but not by protein-hydrochloric acid. Organic acids cause less interference, and lactic acid in the proportion of 0.2 p/m in presence of bile and of NaCl , none whatever. Its action is diminished by accumulation of its products.

The acid chyme, the product of salivary and gastric digestion, passes into the duodenum, where it meets the bile and the pancreatic and enteric secretions, whose alkalinity soon overcomes the acidity. The pepsin is destroyed, peptic digestion ceases, and pancreatic digestion begins. Considering here the proteins of the chyme, this "raw material" for the action of trypsin may contain native and coagulated albumins, acid albuminates, primary and secondary albumoses of both hemi and anti groups, antialbumid and small quantities of peptones. In discussing tryptic digestion, it is important to hold in mind the distinction between that degree of such action for which there is time during the sojourn of the material in the small intestine, and which actually occurs in the body, and the much more complete decomposition of the proteins which is brought about by long-continued action of trypsin at the body temperature. The action of trypsin, continued during several days, is very similar to that of hot mineral acids, producing finally complete disappearance of the biuret

reaction, and "end products" of low molecular weight, and of comparatively simple chemical composition and constitution, which are probably useless for purposes of nutrition; and probably the stage of formation of trypsin-peptones is the limit of "natural" tryptic digestion.

With the change from acidity to alkalinity any native or coagulated albumins and acid albuminates are converted into alkali albuminates, the action of the alkali being accelerated by the enzyme. The alkali albuminates are rapidly converted by trypsin into deuteroalbumoses, without preliminary formation of primary albumoses, which latter, present in the chyme as products of peptic digestion, are also converted into deuteroalbumoses, the heteroalbumoses more slowly than the protoalbumoses. The hemi groups, contained in the deuteroalbumoses A and the thioalbumoses are then split to tryptophane (p. 540) and amido acids, and from the anti groups and pepsin-peptones the trypsin-peptones are derived.

These **antipeptones**, although obstinately withstanding further decomposition by trypsin, are slowly attacked by it, and by sufficiently prolonged autolysis of pancreatic tissue are broken down to products no longer giving the biuret reaction. Siegfried's pepsin-fibrin-peptone α is decomposed by tryptic digestion, splitting off tyrosin and other amido acids, and yielding two antipeptones, **trypsin-fibrin-peptones** α , $C_{10}H_{17}N_3O_5$, and β , $C_{11}H_{19}N_3O_5$, which are acids, giving the biuret but not the Millon reaction, containing no tyrosin group, precipitated by alcohol, and resisting further decomposition by trypsin. On hydrolysis by mineral acids they yield arginin, lysin and glutamic and aspartic acids. Less than 25 per cent of their total nitrogen is contained as basic nitrogen, and the α -acid yields 21.9 per cent of its nitrogen as ammonia and the β -acid 16.1 per cent. The **trypsin-glutin-peptone** β of Siegfried, $C_{19}H_{30}N_6O_9$, itself an acid, on decomposition by HCl yields a basic peptone, $C_{21}H_{30}N_9O_8$, called **glutokyrin**, which gives the biuret reaction, and on further decomposition yields two-thirds of its nitrogen as arginin and lysin, and one-third as glutamic acid and another amido acid, probably glycocoll.

Antialbumid, which is not further decomposed by peptic digestion, produces by tryptic digestion a gelatinous coagulum, which does not give the Millon reaction, and which apparently belongs to the class of **plasteins**, compounds which are peptoids, not giving the biuret reaction, produced by pepsin, trypsin and papayotin from concentrated solutions of albumoses.

Among the products of further tryptic decomposition of the peptones are Fischer's polypeptids, which give the biuret reaction and therefore come within the definition of the peptones, and which are with difficulty decomposed by trypsin into amido acids, which do not

give that reaction. Among these is "Curtius' base," probably hexa-glycylglycin ester, $\text{H}_2\text{N}(\text{NH}.\text{CH}_2.\text{CO})_6.\text{CH}_2.\text{COO}(\text{C}_2\text{H}_5)$, which by tryptic, but not by peptic, digestion yields glycoll, with disappearance of the biuret reaction. As trypsin does not split biuret, oxamid, malonamid or other acid amids, it would appear that the grouping $\text{N}.\text{CH}_2.\text{CO}.\text{N}$ is more truly characteristic of the protein molecule in its response to the biuret reaction than is the grouping $\text{N}.\text{CO}.\text{CO}.\text{N}$ of biuret and the acid amids (p. 407). Another product of peptic and tryptic digestion of globin (p. 660), containing a modified $\text{N}.\text{CH}_2.\text{CO}.\text{N}$ group, and giving the biuret reaction, is leucinimid, or leucin anhydrid, which readily yields the dipeptid leucylleucin. The peptic leucinimid is apparently identical with the synthetic product, but the tryptic leucinimid differs from it in fusing point and in solubility. The polypeptids on decomposition yield aliphatic amido acids: glycoll, alanin, leucin, aspartic and glutamic acids (p. 415), and also phenylalanin and prolin derivatives (p. 511).

The formation of peptones and the further splitting of albumoses and peptones to disappearance of the biuret reaction by pancreatic action do not proceed parallel with each other. The peptonizing action increases with duration of the action, because of the formation of trypsin from the zymogen, but the peptone splitting action diminishes. This is explained by the supposition that the splitting of peptones and albumoses is effected partly by trypsin and partly by another enzyme, which is destroyed by the trypsin. This second enzyme is called **pancreas erepsin** (Vernon), because of the similarity of its action to that of the erepsin of the intestinal mucosa (632). The two erepsins are, however, not identical, for, while the activity of both is increased by an increase of alkalinity to the extent of 0.4 to 1.2 per cent of Na_2CO_3 , at this degree of alkalinity the intestinal erepsin is destroyed, but the pancreatic is not.

The proteids are split by trypsin in the same manner as by pepsin, and their albumin components are digested as native albumins. The nucleins and those nucleoproteids which resist peptic action are decomposed by trypsin with formation, not of nucleins, but of nucleic acids, which are in turn acted upon, but not to the extent of liberation of xanthin bases and a phosphorus acid. The protamin of salmon melt is digested by trypsin, with formation of amido acids and arginin.

After prolonged fasting, on giving food rich in fats, regurgitation of pancreatic juice and bile into the stomach has been observed. The stomach contents then become alkaline and contain notable quantities of active trypsin, and pancreatic digestion then begins in the stomach (Boldireff).

Autolysis, or autodigestion, of an organ is self-digestion of the constituents of the organ after death, with complete exclusion of bac-

terial action. It is supposed to be produced by "autolytic enzymes" contained in the cells, and is particularly active in the liver and pancreas. So far as observed, the action is essentially post-mortem, but whether any similar action occurs during life or not is unknown. In autolysis of the pancreas the products differ somewhat from those produced by tryptic digestion. Guanidin is produced, and the amount of nitrogen separable as ammonia by distillation of the products of decomposition with magnesia is greater than that which is split from the original material as ammonia by hydrolysis by acids, showing that the decomposition has proceeded beyond the stage of formation of amido acids, which is not the case with tryptic digestion. Besides the products of tryptic digestion, oxyphenylethylamin is produced during autolysis, probably resulting from tyrosin by splitting off of carbon dioxid: $(\text{HO})\text{C}_6\text{H}_4.\text{CH}_2.\text{CHNH}_2.\text{COOH} = \begin{smallmatrix} (\text{HO})\text{C}_6\text{H}_4 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \text{NH} + \text{CO}_2$. Uracil and xanthin bases are also produced from the nucleoproteids, and cholin from the lecithins. During six weeks' autolysis a substance called **skatosin**, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2$, is produced (Baum). It is basic, precipitates with phosphotungstic acid, forms a yellow precipitate with bromin water, produces a tetrabenzoyl derivative, gives an odor of skatole when fused with KHO, and appears to belong to the indole group.

Pancreatic diastase, or amylopsin, which may be extracted from the gland tissue after exposure to air, by salicylated water or glycerol, begins to be produced at the end of the first month of infant life. Its action is similar to that of the ptyalin of the saliva, and whether the two enzymes are identical or not is still a mooted question. The action of amylopsin upon cooked starch is energetic, and it also hydrolyses raw starch, more slowly, at $37-40^\circ$. The limit of its action is the formation of maltose, or isomaltose. It does not hydrolyse either maltose, lactose or saccharose further, nor does the pancreatic secretion contain a maltase, a lactase, or a sucrase.

Pancreatic lipase, or steapsin, saponifies the fats with formation of glycerol and fatty acids. The latter, combining with the alkali, form soaps, which aid to emulsify the remaining fat. This enzyme is less resistant than trypsin or amylopsin, and can only be extracted from the fresh gland, not from one which has been exposed to air. Its activity is increased by the presence of bile or of the intestinal secretion. The pancreas also exerts an influence upon the absorption and metabolism of fat other than that by its secretion. After ligation of the pancreatic duct the absorption of fat falls but little below the normal; but after extirpation of the pancreas the fæces contain not only all the fat of the food, but an additional quantity, which excess must originate in the system (Lombroso).

INTESTINAL SECRETIONS.

The intestinal juice, *succus entericus*, is the product of secretion of numerous small glands, including Lieberkühn's follicles and the solitary glands, throughout the intestine, Brunner's glands in the duodenum and upper jejunum, and Peyer's patches in the ileum and lower jejunum, to which may be added constituents apparently formed by the epithelial cells of the duodenum and upper jejunum. The secretion has been obtained in a few cases of intestinal fistula in the human subject, and from animals by the establishment of a "Vella fistula," which is made by resecting a loop of about 2 dm. of intestine, both ends of which are sutured to the abdominal wall, while the continuity of the remainder of the gut is secured by joining the other two ends.

The secretion of Brunner's glands may be obtained individually from a duodenal fistula (Glæssner). It differs from that of the other enteric glands in exerting a marked proteolytic action in faintly alkaline, neutral or acid reaction, with formation of tryptophane. It is alkaline, sp. gr. 1.005–1.020, and small in quantity, about 1 cc. per hour. It has no amylolytic action.

The formation of the enteric secretion is intermittent, begins to be most active about four hours after eating, and continues actively for about three hours thereafter. It may be provoked or greatly increased by electrical or mechanical stimulation. Its quantity is not definitely determined, although 50–125 cc. daily have been obtained from an intestinal fistula in the human subject (Hamburger & Heckma).

The juice obtained from the ileum, freed from mucus by filtration, is thin, yellowish, sp. gr. 1010–1011, and strongly alkaline, the alkalinity being due to carbonates, which cause effervescence on addition of an acid. It contains from 12 to 24 p/m of solids, among which are albumins, a nucleoalbumin and enzymes. Of the enzymes the most active are the **invertins**, maltase and sucrase, which hydrolyse maltose and sucrose to the monosaccharids. Lactase is apparently absent except when the food contains milk sugar. Probably it contains neither amylase, lipase nor proteolytic enzyme. So far as enzyme action is concerned, its function appears to be limited to the inversion of the disaccharids produced by salivary and pancreatic digestion, although it is claimed that a slight amylolytic action has been observed.

Besides the secretin (p. 626) and the enterokinase (p. 627) mentioned above, the epithelial cells of the upper small intestine produce an enzyme, called **erepsin** (Cohnheim), which, although it has no action upon native albumins or histons, rapidly hydrolyses albumoses, peptones and protamins in faintly alkaline or neutral, but not in acid,

reaction, with formation of substances which, like the peptoids, do not give the biuret reaction. It also decomposes casein similarly and splits the nucleic acids. Among the products of its action are arginin, lysin, histidin, leucin, tyrosin and ammonia. It does not further decompose the amido acids. It is destroyed by boiling water, more slowly at 63°. It is not destroyed by acetic acid in one hour, but is by prolonged contact with dilute hydrochloric acid; and alcohol interferes with its action. It is not identical with the enzyme having a similar action, produced by the pancreas. Whether erepsin acts intracellularly (Cohnheim) or extracellularly (Salaskin), or in both ways, is undetermined.

THE BILE.

The bile, being easily obtained from the gall bladder, was early the subject of chemical investigation. It was formerly supposed to be actively concerned in digestion, but it is now known that the digestive action which it exerts is much less important than its excretory function. It has no action whatever upon either proteins or carbohydrates, and its only digestive utility consists in aiding in the saponification and emulsification of the fats, in providing a portion of the alkali required to alkalize the acid chyme, and, indirectly through emulsification of the fats, in acting as a check upon bacterial activity. The bile has no direct antiseptic action, but in its absence the fats, if present in notable amount and being imperfectly emulsified, mechanically protect the proteins from pancreatic digestion and thus reserve them for bacterial fermentation lower in the intestine. In its capacity of emunctory the liver separates from the portal blood, not only poisonous substances introduced from without, but also products of digestion and of bacterial fermentation which would exert toxic actions if permitted to enter the general circulation, and a part of which at least is eliminated in the bile. The bile also contains catabolic products, some of which, being insoluble in aqueous liquids, could not be eliminated by the urine. But the bile is not, like the urine, a pure excretion, because, not only has it a certain degree of utility in digestion, but some of its constituents are modified in the intestine, and the products are reabsorbed, to appear finally in a modified form in the urine.

Human bile has been obtained shortly after death in several instances from executed criminals, and during life in cases of biliary fistulæ consequent upon cholecystostomy. From animals it may be obtained from permanent biliary fistulæ, which cause no disturbance in the nutrition of the animal, with food not too rich in fats. The bile thus obtained from the gall bladder is thicker, more cloudy and of higher specific gravity than that secreted by the liver cells.

The secretion of the bile is continuous, but the quantity produced varies greatly at different times and in different individuals. In the dog the daily production has been found to vary from 2.9 to 36.4 gms. per kilo of body weight. No data are available to show the amount produced in 24 hours by the human subject, although it has been estimated at 500 to 950 gms., and also at 14 gms. per kilo of body weight.

The bile contained in the gall bladder is cloudy, somewhat viscid, alkaline, sp. gr. 1010 to 1040, bitter in taste, with a sweetish after-taste, having a faint, musky odor, particularly perceptible when it is heated, and varying in color from a bright golden-yellow to a dark olive-green. In man it is usually yellow, but sometimes green.

Composition.—Several analyses of specimens of human bile taken shortly after death or from biliary fistulæ, have been made, in which the numerical results have varied within tolerably wide limits and the difference between bladder-bile and hepatic-bile are quite notable. The proportion of solids and water were found to be: Solids, 89.2 to 177.3; water, 910.2 to 822.7 for bladder-bile; and solids, 22.4 to 35.3; water, 977.6 to 964.7 for hepatic-bile. The greater concentration of the bladder-bile, and its greater viscosity, are due in part to the addition of mucus secreted by the bladder, and partly to absorption of water. The solids in bladder-bile consist of: Mineral salts, 0.65 to 0.77 per cent; mucin and biliary pigments, 1.3 to 3.0 per cent; biliary salts, 5.6 to 10.8 per cent; cholesterol, 0.16 to 0.35 per cent; fats, 0.3 to 0.9 per cent; soaps, 0.6 to 1.6 per cent, and lecithins and urea. In hepatic-bile: Mineral salts, 0.73 to 0.99 per cent; biliary pigments, 0.3 to 0.53 per cent; biliary salts, 0.93 to 1.82 per cent; cholesterol, 0.06 to 0.16 per cent; fats and lecithins, 0.02 to 0.15 per cent, and soaps, 0.10 to 0.14 per cent. The mineral salts consist of the chlorids and phosphates of Na, K, Ca, Mg, and Fe, and Na_2CO_3 . Copper is always present in the liver, zinc frequently, and both may be found in the bile. The mucin is partly a true mucin, a glucoproteid, and partly a nucleoalbumin. Urea is present in small amount only, but is found in large quantity in the bile of the shark.

Biliary Salts.—The bile of all animals contains the salts of conjugate amido acids peculiar to this secretion. They vary in composition in different animals, but may be classed in two groups, the members of one of which (glycocholic series) yield glycocoll, or amido-acetic acid (p. 413) when boiled with acids, while those of the other (taurocholic series) yield taurin, or amido-isethionic acid (p. 421) under like treatment. The other product of the decomposition is, in both cases, **cholic acid**, $\text{C}_{24}\text{H}_{40}\text{O}_5$, whose constitution is undetermined beyond the fact that its molecule contains one CHOH group, two CH_2OH groups and one COOH group. It crystallizes in octahedra or in rhombic prisms, is easily soluble in alcohol, requires 4,000 parts of cold, or

750 of hot water for its solution, is insoluble in ether, and becomes cloudy on exposure to air. In alcoholic solution it is dextrogyrous, $[\alpha]_D = +35^\circ$. Its Na and K salts are readily soluble in water; and their solutions are precipitated by lead acetate, or by barium chlorid. Cholic acid is easily oxidized or reduced. On oxidation it first loses H_6 to form **dehydrocholic acid**, $C_{24}H_{34}O_5$, a crystalline, monobasic acid, sparingly soluble, which does not respond to the Pettenkofer reaction. This then takes up oxygen to form **bilianic acid**, $C_{24}H_{34}O_8$; and this is then converted into a mixture of **cholesteric acid**, $C_{12}H_{16}O_7$, **pyrocholesteric acid**, $C_{11}H_{16}O_7$, **cholanic acid**, $C_{20}H_{28}O_6$, and fatty acids. By reduction, it yields, first, **deoxycholic acid**, $C_{24}H_{40}O_4$, which also exists in putrid bile; and then **cholylic acid**, $C_{24}H_{40}O_2$. Two other acids, related to cholic acid, have been derived from human bile, one **choleic acid**, $C_{24}H_{40}O_4$, possibly identical with deoxycholic acid; the other **fellic acid**, $C_{23}H_{40}O_4$. By boiling with acids, and during intestinal fermentation, cholic acid loses H_2O and is converted into an anhydrid, **dyslysin**, $C_{24}H_{38}O_3$, which is amorphous, and insoluble in water and in alkalies.

Besides the biliary acids of the glycocholic and taurocholic groups, an acid has been obtained from the bile of the shark (Hammarsten) which possibly represents a third group. It contains sulfur, and on hydrolysis by HCl it yields sulfuric acid. It therefore probably has a constitution similar to that of the sulfo-conjugate acids of the urine.

Cholic acid and the conjugate acids containing it give the **Pettenkofer, or furfurole, reaction**: on addition of a few drops of cane-sugar solution and then of concentrated H_2SO_4 , the temperature being kept down to about 70° , the solution becomes turbid, and soon assumes a fine purple color. The colored liquid, sufficiently diluted with acid, gives a spectrum of two bands, one at F, the other between D and E, near to E. Many other substances give the Pettenkofer reaction: Albumins, phenols, polyatomic alcohols, morphin, oleic acid, salicylic acid, etc.; therefore, it is only indicative of the presence of bile salts, if these have been separated by extraction of the dried substance by alcohol and precipitation by ether. With H_2SO_4 alone at the ordinary temperature, solutions of the biliary acids are colored reddish-yellow, with a green fluorescence.

The biliary acids are obtained from the bile, dried with animal charcoal, by extraction with strong alcohol and precipitation by addition of ten volumes of anhydrous ether. On standing, the gummy precipitate of sodium salts becomes crystalline in whole or in part. These are collected and dissolved in water. Neutral lead acetate is added to the solution, which precipitates lead glycocholate; and from the filtrate lead-taurocholate is precipitated by ammonia. The separated lead salts, suspended in water, are decomposed by H_2S , the aqueous solution

filtered off, and evaporated to dryness. The acids are then dissolved in small volumes of absolute alcohol and precipitated by anhydrous ether, and purified by repetition of solution in alcohol and precipitation by ether.

Glycocholic Acid— $C_{26}H_{43}NO_6$ —predominates, in its sodium salt, in human bile and in that of the ox, but is absent in that of the carnivora. It crystallizes in silky needles, soluble in 300 parts of cold, and 120 parts of hot water, easily soluble in alcohol, insoluble in ether, which precipitates it from its alcoholic solution. Its taste is at the same time bitter and sweet. In alcoholic solution it is dextrogyrous $[\alpha]_D = +29^\circ$. Its Na salt is much more soluble in water than the free acid, and its solutions are precipitated by $(C_2H_3O_2)_2Pb$, $CuSO_4$, Fe_2Cl_6 , or $AgNO_3$. When heated with alkalis or dilute acids, glycocholic acid is decomposed into cholic acid and glycocoll, $C_{26}H_{43}NO_6 + H_2O = C_{24}H_{40}O_5 + CH_2(NH_2).COOH$. Heated with concentrated H_2SO_4 it loses water to form **cholonic acid**, $C_{26}H_{41}NO_5$.

Taurocholic acid— $C_{26}H_{45}NSO_7$ —exists, as its sodium salt, in human bile and in that of the carnivora, in much less amount in that of the herbivora. It is very soluble in water and in alcohol, insoluble in ether. It crystallizes with difficulty in silky needles by precipitation of its solution in absolute alcohol by anhydrous ether. These crystals rapidly deliquesce to an amorphous, resinous mass on exposure to air. Its taste is bitter and sweet. In alcoholic solution it is lævogyrous, $[\alpha]_D = -24.5^\circ$. Its sodium salt is very soluble, and its solutions are not precipitated by the salts which precipitate with glycocholic acid, but it is precipitated by basic lead acetate. Heated with alkalis or dilute acids, or even on evaporation of its aqueous solution, taurocholic acid is decomposed into cholic acid and taurin: $C_{26}H_{45}NSO_7 + H_2O = C_{24}H_{40}O_5 + CH_2(NH_2).CH_2.SO_3H$. Solutions of taurocholates and of glycocholates dissolve cholesterol and alkaloids, if the salt be in excess. They emulsify oils and peptone solutions. They precipitate albumins and albumoses.

Biliary Pigments.—The bile of all animals contains peculiar pigments, which are derivatives of the blood-coloring matter. The most important are **bilirubin** and **biliverdin**.

Bilirubin, $C_{32}H_{36}N_4O_6$, occurs in its sodium salt in the bile of all vertebrates, particularly in that of the herbivora, in the intestinal contents, in biliary calculi (as its calcium salt), and, pathologically, in the urine, blood, and tissues, and, crystallized as "hæmatoidin," in old extravasations of blood. It forms either an amorphous, reddish-yellow powder, or scarlet crystals, or, when crystallized by spontaneous evaporation of its chloroform solution, reddish-yellow rhombic plates. It is insoluble in water, sparingly soluble in alcohol or in ether, readily soluble in chloroform, carbon disulphid, benzene, and in alkaline solu-

tions. Towards bases it behaves like a phenol, forming soluble salts with the alkali metals, and insoluble or sparingly soluble ones with those of the alkaline earths. It has great pigmentary power, but its solutions give no spectrum. If, however, its alkaline solutions be treated with ammonia in excess and zinc chlorid, they change in color to deep orange and then to green, and then give a spectrum of a single band near C, and between C and D. When reduced by zinc dust or by HI, bilirubin yields hæmopyrrole (p. 510). By the action of sodium amalgam upon a solution of bilirubin in weak alkali the liquid becomes opaque, and, after two or three days, turns brown, when upon addition of HCl, it turns red and deposits brown flocculi of a substance which closely resembles, if it is not identical with, the stercobilin of the fæces and the urobilin of the urine. This substance, which is called **hydrobilirubin**, $C_{32}H_{40}N_4O_7$, is formed from bilirubin by hydrogenation, followed by oxidation of its solution in air: $C_{32}H_{36}N_4O_6 + 3H_2 + O_2 = C_{32}H_{40}N_4O_7 + H_2O$. Solutions of bilirubin salts on exposure to air soon become green from formation of biliverdin by oxidation.

The reactions of bilirubin are utilized for the detection of bile in the urine and elsewhere. They are: (1) *Gmelin's reaction*—The liquid examined is floated upon the surface of nitric acid containing a little nitrous acid, when a series of colors, green, blue, violet, and reddish-yellow, are produced at the union of the two layers, of which the green is the most marked. There must be no alcohol present. Limit 1:80,000. This reaction depends upon a progressive oxidation, with formation of the following products: (a) **biliverdin**; (b) **bili-cyanin**, whose neutral solutions are of a fine blue color, with red fluorescence, and whose alkaline solutions are green, and give a spectrum of three bands, one between C and D, nearer to C, one over D, and the third near to E, between E and F; (c) a red pigment, the nature of which has not been determined; (d) **choletelin**, a brownish-yellow pigment, whose alcoholic solution gives a spectrum of one band between E and F. (2) *Hammarsten's reaction*—The reagent used is made by mixing 1 vol. HNO_3 with 19 vols. HCl, and letting the mixture stand until it is yellow. A colorless liquid is formed by mixing 1 vol. of this reagent with 4 vols. of alcohol, which is colored intensely green by a trace of bilirubin. (3) *Huppert's reaction*—The liquid is treated with barium chlorid and ammonia; and the precipitate formed is washed with water, and covered while still moist in a test-tube with alcohol and acidulated with hydrochloric acid. The mixture is then heated to boiling, when, in presence of bilirubin, it becomes emerald green.

Biliverdin— $C_{32}H_{36}N_4O_8$ —accompanies bilirubin in bladder-bile, but not in hepatic-bile, and is most abundant in green biles. It is amorphous, insoluble in water, ether or chloroform, soluble with a

green color in alcohol and in glacial acetic acid, or with a brown color in alkalies. It is precipitated from its solutions by acids and by salts of Ca, Ba, and Pb. It responds to the tests for bilirubin. Its alcoholic solution, treated with ammoniacal ZnCl_2 , shows a green fluorescence. Reducing agents convert it into bilirubin; oxidizing agents into biliverdic acid, $\text{C}_8\text{H}_9\text{NO}_4$. It is best obtained by oxidizing bilirubin.

Bilifuscin is a brown, amorphous pigment, occurring in biliary calculi and in putrid bile, which is soluble in alcohol and in alkalies, insoluble in water, ether or chloroform. It does not respond to the Gmelin reaction. **Biliprasin** is the name given to a green pigment occurring in biliary calculi, which is probably a mixture or combination of bilirubin and biliverdin. **Bilihumin** is a brown, amorphous pigment, obtained from biliary calculi, which is insoluble in alcohol, ether or chloroform, and which does not give the Gmelin reaction.

Cholesterol — Cholesterin — $\text{C}_{27}\text{H}_{45}\text{OH}$ — is a monoatomic alcohol of unknown constitution, which exists normally in almost every animal tissue and fluid, in many in very minute quantity, most abundantly in the bile, nerve tissues, intestinal contents, fæces, and in sebum and wool-fat. In pathological products it is frequently an abundant constituent, and is met with in biliary calculi, certain brain tumors, atheromatous degenerations, pus, the fluids of cysts, hydrocele, etc., as well as in cancerous and tubercular deposits, and in the lens in cataract. In some of these situations it exists free, in its peculiar, crystalline form of very thin, colorless, rhombic plates, while in others it is in combination in the form of its esters. It also exists in the vegetable world, widely distributed, notably in peas, beans, olive-oil, wheat, etc.

Cholesterol is insoluble in water, in alkalies, or in dilute acids, difficultly soluble in cold alcohol, readily soluble in hot alcohol, ether, benzene, acetic acid, glycerol, and solutions of the biliary acids. It is odorless and tasteless; f. p. 145° ; sp. gr. 1.046. It is lævogyrous, $[\alpha]_D = -31.6^\circ$, in any solvent. It combines readily with volatile fatty acids, and from its solution in glacial acetic acid a compound, $\text{C}_{27}\text{H}_{45}\text{O} \cdot \text{C}_2\text{H}_3\text{O}_2$, crystallizes in fine curved needles, which are decomposed on contact with water or alcohol. When heated with acids under pressure, it forms true esters, some of which also exist in wool-fat, and in "lanolin," derived therefrom. By oxidation it yields a series of acids, from **cholesteric acid**, $\text{C}_{26}\text{H}_{44}\text{O}_4$ —not identical with the acid of the same name derived from cholic acid (p. 635)—to **trioxycholesteric acid**, $\text{C}_{26}\text{H}_{44}\text{O}_7$.

Cholesterol may be recognized by the following characters: (1) Its crystalline form, thin rhombic plates, usually having one obtuse

angle missing. (2) If these crystals be moistened with dilute H_2SO_4 (1:5) they are colored, first bright carmine, and then violet, beginning at the borders. If iodine solution be now added, the color changes to bluish-green, then to blue. (3) When H_2SO_4 is added to a solution of cholesterol in chloroform, the liquid is colored purple, changing during evaporation to blue, green and yellow (Salkowski). (4) If acetic anhydride be added to a chloroform solution of cholesterol, and then a drop or two of concentrated H_2SO_4 , the mixture becomes first red, then blue, and finally green (Liebermann-Burchard). (5) When a mixture of 2-3 vols. of H_2SO_4 or HCl and one vol. of dilute Fe_2Cl_6 solution is evaporated upon cholesterol, a residue is obtained which is at first purple, then violet (Schiff). (6) When moistened with concentrated HNO_3 and the liquid evaporated, cholesterol leaves a yellow residue, which is colored dark orange-red by NH_4HO or NaHO (see Murexid Reaction, p. 530). (7) Pure, dry cholesterol, moistened with propionic anhydride and dried and fused, leaves a residue which on cooling becomes first violet, then blue, green, orange, carmine-red, and finally copper-colored (Obermüller).

Isocholesterol has the formula $\text{C}_{26}\text{H}_{48}\text{OH}$, formerly assigned to cholesterol. It occurs in wool-fat, accompanying cholesterol, from which it differs in its f. p. = 138° (280.4°F.), and in not responding to the Salkowski reaction.

Origin and Destiny of the Biliary Constituents.—The biliary salts are produced in the liver, and do not preëxist in the blood. This is proven by the facts that they do not accumulate in the blood after extirpation of the liver in frogs, and that in dogs they are absorbed by the lymphatics of the liver and carried to the blood by the thoracic duct after ligation of the ductus choledochus, but they do not appear in the blood after ligation of both ductus choledochus and thoracic duct. Although the immediate antecedents of the biliary salts are not known, they are probably formed by union of their constituents, which are derived from different sources. Cholic acid, containing neither nitrogen nor sulfur, and containing both alcoholic and carboxyl groups, is in all probability derived from a carbohydrate, or possibly from the fats. There is also evidence that it may be derived from cholesterol. If defibrinated blood holding finely divided cholesterol in suspension and glycocholate in solution be injected into the portal vein of a dog, the blood of the hepatic veins responds to Pettenkofer's reaction, although it did not do so previous to the injection. The action would involve an oxidation and a synthesis. When cholic acid is injected into the circulation of dogs the formation of taurocholic acid is temporarily increased. Glycocholate and taurin both contain nitrogen, and the latter sulfur also. They are, consequently, derived from the proteins. Glycocholate is one of the principal products

of hydrolysis of collagen and other albuminoids, and is a decomposition product of most proteins. Most probably taurin originates from the proteins through cystin and cysteic acid (p. 421, 422). Although the sulfur content of the bile is not increased by administration of cystin alone, it is increased by administration of cystin and cholic acid. The biliary salts are not reabsorbed unchanged from the intestine under normal circumstances, or, at all events, not in any notable quantity. Solutions of these salts, when injected into the circulation, are rather active poisons. In small doses they cause diminution in the frequency of the pulse and of the respiratory movements, lowering of the temperature and arterial tension, and disintegration of the blood-corpuscles. In large doses (2-4 gm. to a dog), they produce the same effects to a more marked degree, and, further, epileptiform convulsions, black and bloody urine, and death. Similar effects, complicated with others referable to the biliary pigments, are observed when, in consequence of obstruction of the bile duct, the bile is absorbed through the lymphatics. These effects do not follow the injection of the products of decomposition of the biliary acids, except cholic acid, and with that the symptoms are much less marked. Nor are the biliary salts found as such in the fæces, except that these occasionally contain glycocholic acid, but never taurocholic acid, which is more readily decomposed. Sometimes cholic acid or, more frequently, dyslysin occurs in the fæces, but not glycocholl or taurin. The decomposition of the biliary salts which occurs in the intestine is due to fermentative (bacterial) action, as the contents of the lower intestine in the foetus contain notable quantities of biliary salts. That the taurin resulting from the decomposition is reabsorbed is demonstrated by the fact that it appears in the urine, partly in its own form, its sulfur partly oxidized to sulfates, and partly as taurocarbamic acid, formed by the union of taurin and carbamic acid: $C_2H_7NSO_3 + CO_2NH_3 = C_2H_8N_2SO_4 + H_2O$. Equally direct proof of the reabsorption of glycocholl is not at hand; but the ready formation of uric acid (p. 529) and of hippuric acid (p. 479) from glycocholl render it probable that the latter substance is an intermediate product in the formation of the other two, in part at least, as well as of urea in the economy.

The **biliary pigments** are also formed in the liver, and do not preëxist in the blood, although bilirubin at least may be formed in other parts of the body, and has been found in old extravasations of blood, and in the placenta. The formation of these pigments in the liver is proven by the following facts: in pigeons, the biliary pigments make their appearance in the blood in five hours after ligation of the bile-ducts; but if the blood-vessels of the liver are ligated at the same time, no pigments appear in the blood or tissues in 24 hours. In geese, poisoned with hydrogen arsenid, the biliary pig-

ments appear in the urine in large quantity; but if the liver have been extirpated before the poisoning this does not occur.

The parent substance of the biliary pigments is undoubtedly the blood coloring matter. If hæmoglobin in solution be injected into the circulation of an animal in small quantity, the amount of bilirubin produced is increased, but the urine contains neither bile- nor blood-pigment, nor does jaundice result. If the quantity of hæmoglobin injected be increased progressively, at first so-called hæmatogenic icterus is produced, from reabsorption of the bilirubin, produced in excessive amount, by the hepatic lymphatics, and the bile-pigment, but no blood pigment, appears in the urine. Finally, with larger quantities of hæmoglobin, jaundice, choluria and hæmoglobinuria all result. A similar condition, due to the same cause, is observed in poisoning by hydrogen arsenid and by phosphorus, in which there is extensive disintegration of red blood-corpuscles, followed by solution of the liberated hæmoglobin in the plasma, and the appearance of the symptoms above noted. The chemical relationship between bilirubin and certain derivatives of hæmoglobin is very close. Indeed, bilirubin is identical with hæmatoidin, which is found in old blood stains, and, in the crystalline form, in old extravasations of blood. Bilirubin is also isomeric with hæmatoporphyrin, a pigment normally present in the urine in small amount, and notably increased therein in poisoning by sulfonal. The relation between hæmatin and bilirubin is shown by the equation: $C_{32}H_{32}N_4FeO_4 + 2H_2O = C_{32}H_{36}N_4O_6 + Fe$, which may, in some modified form, indicate the method of formation of the biliary pigment. The iron thus liberated has been accounted for only in part. The bile always contains iron, principally in the form of ferric phosphate, to the proportion of from 0.04 to 0.115 p/m. But the correspondence between the amount of iron present and the amount of bilirubin formed, which the above equation would call for, has not been found to exist. For 100 parts of bilirubin present in the bile, 1.4 to 1.5 parts of iron have been found, whereas an equivalent quantity of hæmatin would yield 9 parts. Moreover, in poisoning by hydrogen arsenid, in which there is an increased formation of bile pigment, no corresponding increase in the amount of iron in the bile has been observed. Undoubtedly the iron thus unaccounted for in the bile goes to the formation of the iron-containing proteins of the liver cells, from which hæmoglobin may probably be regenerated (p. 679).

There is no correspondence in the observed variations in the quantities of biliary salts, and of biliary pigments formed. As these variations take place independently of each other, the processes of formation of the two classes of substances may be considered as being distinct from each other.

The biliary pigments are not reabsorbed unchanged in health. When they are pathologically (icterus, phosphorus poisoning) they stain the skin and tissues, and make their appearance in the urine. The coloring matter of the fæces, stercobilin, and at least one of those of the urine, urobilin, are derived from bilirubin (p. 725).

Cholesterol exists in the protoplasm of all cells, and is particularly abundant in nerve tissues. In analyses of brain substance it has been found to constitute a large portion of the solid constituents of both white and gray matter, particularly of the former. It is constantly present in the fæces in its own form or in that of a derivative (koprostearin, stercorin), and only appears in the urine in chyluria. It is, in all probability, a catabolic product produced principally in nervous tissues.

Biliary Calculi.—Calculi are frequently met with in the gall bladder after death, and the smaller ones often pass into the intestine during life. These calculi may be divided into three classes, according to the nature of their chief constituents: (1) *Pigmentary calculi*, consisting chiefly of the several pigments mentioned above, combined with calcium, and sometimes associated with calcium salts. They are usually multiple, sometimes very numerous. They are yellow, green, brown or black in color; sometimes rounded and nodulated upon their surfaces, more usually having flattened surfaces, and more or less perfect geometrical shapes, produced by attrition one against the other. In cattle these stones are sometimes found as large as a walnut. (2) *Cholesterol calculi*, consisting almost entirely of cholesterol. They are usually single, rounded and polished, having a nacreous appearance and an ovoid outline. They may measure nearly an inch in their longer diameter. (3) *Calcic calculi* are much more rare in the human subject than the other two forms. They consist mainly of tricalcic phosphate and calcium carbonate.

CHEMICAL CHANGES OCCURRING IN THE INTESTINE.—ABSORPTION.

The changes which the constituents of the food undergo in the alimentary canal are the sum of the effects produced by the several digestive secretions, modified by their influences upon each other's actions, and the chemical reactions set up by bacterial life, constantly present and active. The changes in the organic food-constituents, carbohydrate, fatty and protein, are briefly the following:

Carbohydrates.—The amylolytic action of the ptyalin of the saliva upon hydrated starch is arrested by the acid reaction of the gastric contents, but may continue for some little time in the stomach in the interior of difficultly permeable masses of starchy foods, particularly as a certain degree of acidity is required to arrest the action. But

once arrested, it is not reëstablished, so far as salivary action is concerned, when the reaction returns to alkaline in the intestine. In the intestine the powerful diastatic action of the pancreatic enzyme, favored by the presence of the bile, takes the place of salivary action and continues the amylolytic hydrolysis through amylodextrin, the erythrodestrins and achroödextrins to the formation of disaccharids. Glycogen is also decomposed to maltose and isomaltose. Inversion of the disaccharids, cane-sugar, milk-sugar, maltose and isomaltose, is effected by the invertins of the intestinal secretion, and also by bacterial action. Even cellulose, if finely divided, is to some extent converted into soluble derivatives in the intestine, probably by bacterial action.

Bacterial action in the alimentary canal is exerted chiefly upon the carbohydrates in the small intestine, and upon the proteins in the large intestine. Normally bacterial activity is held in check in the stomach by the germicidal action of the acid of its secretion, and it is only when this is in abeyance, as in anachlorhydria, that gastric fermentations occur. But the entire intestinal tract is inhabited by a bacterial flora of considerable variety, and active bacteria have been found as high as 2 cm. in the pancreatic duct in dogs. In the large intestine bacteria are much more numerous than in the small intestine, and their numbers and activity are inversely proportionate to the activity of peristalsis. It has been claimed that the floræ of the two divisions of the gut are distinct, that the bacteria of the small intestine find entrance by the mouth, those of the large intestine by the anus, and that neither pass the ileo-cæcal valve. It has also been claimed that the presence of bacteria in the intestine is essential to life. As it is impossible to disinfect the intestine, once bacteria have found lodgment therein, without at the same time destroying the life of the host, this question can only be determined by observations upon animals born and reared aseptically. Although the results are not entirely conclusive, observations made with chicks and with guinea-pigs, the latter born by cæsarian section, appear to show that, while the development of the aseptic young is not radically interfered with, it is not so rapid as that of the control animals. Bacterial decomposition of the carbohydrates takes place almost entirely in the small intestine. In its earlier stages, with starches, dextrins and disaccharids, the products are the same as those formed by the digestive enzymes. But, particularly with cellulose, which escapes digestion by the secretions of the host, the changes readily proceed further by alcoholic, acetic, lactic and butyric fermentations set up by the corresponding ferments. The contents of the lower ileum contain alcohol, and are acid from the organic acids mentioned, as well as succinic and paralactic acids and biliary acids. In butyric fermentation,

whether direct from glucose or through lactic acid, nascent hydrogen is produced: $C_6H_{12}O_6 = C_4H_8O_2 + 2CO_2 + 2H_2$, which effects certain reductions occurring in the intestine, as that of bilirubin. Although the saliva of dogs contains no ptyalin, these animals after extirpation of the pancreas are still capable of assimilating from 40 to 70 per cent of starch ingested, whose hydrolysis must be accomplished by bacterial action or by that of enteric secretions, unless, as has been claimed, the stomach of these animals secrete an amylase acting in acid solution.

When excessive quantities of sugars are taken, absorption does not keep pace with inversion, bacterial fermentations become more active, and the irritating quality of the acids, produced in abnormally large amount, causes increased peristalsis and diarrhœa. Starch, when taken in excess, does not produce these results, but the excess is eliminated unchanged in the fœces.

Polysaccharids can only be absorbed after hydrolysis at least to the stage of disaccharids. Lactose and saccharose do not occur normally in the blood, and when injected into the circulation are not utilized, but are eliminated in the urine as foreign material. To be of service, therefore, the hydrolysis must proceed to the stage of monosaccharids, either in the intestine or in its epithelium, through which the products of carbohydrate digestion are absorbed into the blood. The absorption of glucose, which requires no preliminary digestive treatment, is more rapid than that of the disaccharids, and of the latter, maltose and saccharose are more rapidly inverted and the products absorbed than is the case with lactose.

Fats.—The only known chemical change which the fats undergo during digestion is a not very abundant saponification to glycerol and fatty acids by the pancreatic enzyme, and possibly also by a gastroteapsin. The liberated fatty acids in part combine with the alkali of the pancreatic juice and the bile to form soaps, which aid in the conversion of the remainder of the fats into a fine emulsion, in which form they are absorbed through the lacteals and thoracic duct into the blood. A small proportion of fat is also saponified in the lower small intestine by bacterial action, and by the same agency the lecithins are split to glycerophosphoric acid, cholin and fatty acids.

The glycerol, fatty acids and soaps resulting from the hydrolysis of the fats and lecithins, and the glycerophosphoric acid from the lecithins are in great part absorbed through the epithelium of the small intestine, and are probably utilized in the synthetic regeneration of fats in the organism. The cholin from the lecithins is decomposed by bacterial action into CO_2 , CH_4 and NH_3 .

The degree of perfection of absorption of fats may be estimated by determining the "loss," i. e., the fraction of the ingested fat present

in the *faeces*. This "loss" does not represent strictly the amount of ingested fat which has escaped absorption, as appreciable quantities are discharged into the intestine with the secretions and epithelium. The loss is the greater as the fusing point of the fat is higher. Thus with olive oil it is 2.3 per cent, with mutton tallow, f. p. 49° , 7.4 per cent, and with pure stearin, f. p. 60° , 90 per cent. When the loss exceeds 30 per cent the existence of disturbance of fat assimilation may be suspected. With excessive peristalsis the loss may be 40 per cent with normal secretion of bile and pancreatic juice. With uncomplicated exclusion of bile from the intestine it reaches 45 per cent; with exclusion of pancreatic juice and partial exclusion of bile 80 to 90 per cent; in *icterus* 80 per cent; and in disease of the pancreas 60 per cent.

Proteins.—The chyme, more or less strongly acid in reaction, and rich in albumoses, acid albuminates, and pepsin-peptones, the products of peptic digestion, is greatly modified shortly after its passage into the duodenum, where an entirely different series of processes is begun. The albumins and albumoses of the gastric contents are precipitated by the bile in acid, not in alkaline reaction; that is, by the free biliary acids, and notably by taurocholic acid, but not by the biliary salts. Peptones are not so precipitated. But the protein precipitate formed by the bile is redissolved by an excess. It is doubtful whether this precipitation occurs to any considerable extent in the human subject, in whom the alkalinity of the bile and pancreatic secretion, discharged into the intestine by a common opening, soon overcomes the acidity of the chyme.

When the reaction in the duodenum changes from acid to alkaline peptic digestion ceases, and the more energetic tryptic digestion begins. This, supplemented by the action of erepsin, results in the breaking down of the albumins, acid albuminates, albumoses and pepsin-peptones to trypsin-peptones, and finally to products no longer responding to the biuret reaction. These changes occur principally in the small intestine, and are not interfered with by the acids produced by fermentation of the carbohydrates, notwithstanding the acid reaction which they produce in the lower small intestine. It is also in the small intestine that the greatest absorption of the products of digestion of the proteins takes place through the intestinal mucosa into the blood. Obviously the utility of protein food is to furnish material for the formation of the constituents of similar nature of the fluids and tissues of the organism. We have seen that the processes of digestion bring about a radical breaking down of the protein molecule into products far removed from it in complexity of structure. In precisely what form, what stage of decomposition, these products are absorbed, and how and where they synthetically regenerate other protein molecules,

are important questions for future investigation. It is known that native or denatured albumins may be absorbed from the intestine in small amount, and albumoses have also been detected in minute quantity in the blood, but these observations entirely fail to afford quantitatively an explanation of the mechanism of the absorption of the products of protein digestion, or of the reconstruction of the protein molecule. On the other hand, it has been demonstrated that dogs can be maintained in perfect nutrition, and in nitrogenous equilibrium when fed upon the products of tryptic digestion, carried to disappearance of the biuret reaction.

As the entire quantity of protein taken with the food is not simultaneously attacked by the digestive agents, they and their products may be found in all the stages of digestion at different points throughout the small intestine, and unaltered native albumins along with their products, not only pass the ileo-cæcal valve, but may be discharged, as waste, in the fæces.

In the large intestine, whose peristalsis is comparatively sluggish, and the reaction of whose contents is usually alkaline, bacterial action, different in kind from that which occurs in the small intestine, takes place. While the small intestine is the seat of fermentation of the carbohydrates, putrefaction of the proteins occurs almost exclusively in the large intestine. This is most intense in the upper part of the gut, and diminishes downwards, as water is absorbed from the intestinal contents, which assume an increasing firmness of consistency. The products of intestinal putrefaction are the same as those formed in the same manner outside of the body, those of anærobic putrefaction predominating. These products include albumoses and peptones, amido acids of the glycocoll and aspartic series, tyrosin, tryptophane, volatile fatty acids, mercaptan, hydrogen sulfid, carbon dioxid, ammonia, methane, hydrogen, and certain products of decomposition of tryptophane and tyrosin which are characteristic of anærobic putrefaction, and which exert more or less pronounced toxic actions. These are indole (p. 539), skatole, and skatole- α -carboxylic acid, products of decomposition of tryptophane; and phenol, paracresol and intermediate products from decomposition of tyrosin. These anærobic products are in part discharged in the fæces, to which they communicate their stercoraceous odor. In part they are reabsorbed and, after oxidation, appear in the urine in conjugate combination, either as ester sulfates or as conjugate glucuronates (p. 732). Indole and skatole are oxidized, after absorption, to phenolic derivatives; indole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH} \\ \text{NH} \end{smallmatrix}\rangle\text{CH}$, to indoxyl, or β -oxyindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix}\rangle\text{CH}$, and skatole, or β -methylindole, to skatoxyl, or α -oxy- β -methylindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{C(CH}_3\text{)} \\ \text{NH} \end{smallmatrix}\rangle\text{COH}$, which then combine with sulfates or with

glucuronates. Skatole- α -carboxylic acid, $\text{C}_6\text{H}_4\text{--}\langle\text{C}(\text{CH}_3)\text{--}\rangle\text{C.COOH}$, is formed by combination of skatole and carbon dioxid. In the formation of p-cresol and of phenol, tyrosin, or p-oxyphenyl- α -amidopropionic acid, $(\text{OH}).\text{C}_6\text{H}_4.\text{CH}_2.\text{CHNH}_2.\text{COOH}$, is first deamidated to p-oxyphenylpropionic acid, $(\text{OH}).\text{C}_6\text{H}_4.\text{CH}_2.\text{CH}_2.\text{COOH}$; this is oxidized to p-oxyphenylacetic acid, $(\text{OH}).\text{C}_6\text{H}_4.\text{CH}_2.\text{COOH}$, which, by loss of carbon dioxid, forms p-cresol, $\text{HO.C}_6\text{H}_4.\text{CH}_3$. The cresol by oxidation yields phenol, which by further oxidation forms the o- and p-diphenols, hydroquinone and pyrocatechin, all of which occur as sulfoconjugate compounds in the urine. The amount of the indole derivatives eliminated in the urine affords an index of the extent of reabsorption of the products of intestinal bacterial action occurring at the time. Certain constituents of the digestive secretions are themselves modified by bacterial action. Thus the biliary pigments are reduced to stercobilin or urobilin, and the biliary acids are split into their components, which suffer further change.

Intestinal Gases.—The gases of the intestine consist largely of nitrogen, derived from swallowed air. Oxygen exists only in very small amount, having been absorbed either by the host or by the bacteria. Carbon dioxid is constantly present in notable amount, produced by putrefaction of the proteins, by fermentative decomposition of the carbohydrates, and by neutralization of the carbonates of the bile and pancreatic secretion. Hydrogen is formed by bacterial growth. Minute quantities of hydrogen sulfid resulting from decomposition of the proteins, and of methane, from decomposition of both proteins and carbohydrates, are also present.

Fæces.—The fæces contain (1) indigestible material contained in the food: cellulose, gums, resins, chlorophyll, keratin, hæmatin; (2) excess of digestible material not utilized: starches, fats, shreds of muscular tissue, coagulated casein, etc.; (3) unabsorbed products of partial digestion: albumoses, peptones, fatty acids, amido acids, etc.; (4) morphological elements from the glands and intestinal mucosa, more or less altered; (5) organic substances derived from the secretions discharged into the intestine: mucins, nucleoproteids, fats, cholesterol, cholic acid, dyslysin, stercobilin; (6) products of bacterial action: acids of the acetic, oxalic and lactic series, amido acids of the glycocoll and aspartic series, tyrosin, phenols, indole, skatole and their derivatives; (7) catabolic products: urea, uric acid, xanthin bases; (8) mineral substances derived from the food or from the secretions: water, earthy phosphates and sulfates, ammonio-magnesian phosphate, silicic acid, silicates, and the usual soluble salts; (9) bacteria and their detritus. Exceptionally also entozoa and their ova, gall-stones, intestinal concretions, or insoluble residues of medicinal substances may be present.

The amount of the fæces depends principally upon the amount of indigestible material taken with the food. It is therefore greater with the herbivora, whose food contains a large proportion of cellulose, only a small fraction of which is utilized, than in the carnivora. In man it is usually from 100 to 200 grams per diem, but may be 500 gms. with a vegetable diet, and may be reduced to less than one-quarter of the normal amount with a diet from which cellulose and other useless material is excluded. Normally, nearly one-third of the weight of the dried fæces consists of bacteria and their detritus. The consistence of the fæces depends upon the amount of water present. The reaction of the fæces of adults is usually faintly alkaline, the acidity of the acids produced by bacterial action having been more than neutralized by the ammonia and amins formed by ammoniacal fermentations. Sometimes, however, with a diet rich in carbohydrates, normal fæces may be neutral or even acid in reaction. In nursing infants, in whom a considerable quantity of lactic acid is formed from the milk-sugar, the reaction is acid. The normal color of the fæces is due to stercobilin (hydrobilirubin), derived from the bile-pigments. When the bile is deficient, the fæces are pale in color, and contain a large quantity of fat. Pale-colored, or acholic, stools may, however, be passed, in which the amount of fat is not excessive, when there is no hepatic disturbance, and, probably, the bile-pigments are converted into leuco, or colorless, derivatives. The fæces are sometimes almost black in color, either from the presence of hæmatin or hæmatoidin after hemorrhages, or from the presence of dark-colored metallic sulfids after administration of the salts of iron, bismuth or lead. When these sulfids are present they frequently deposit as heavy, dark-colored powders at the bottom of the vessel. The fæcal odor is largely due to indole and skatole, somewhat modified by the odors of ammonia, of hydrogen sulfid and of mercaptans.

Chemical analysis of fæces is rarely resorted to for clinical information, except when the amount of fat is of interest in connection with hepatic or pancreatic disease, but in investigations of metabolism the results of quantitative determinations of various constituents of the fæces are data essential to the inquiry. The nature of the constituents to be determined varies with the character of the problem under examination, but those most frequently of interest are nitrogen and fats. Both are determined from the dried fæces, the former by the Kjeldahl method, the latter by extraction with ether, and, if necessary, determination of true fat in the mixture of fat, lecithins and cholesterol which constitutes the "crude fat" of the ether extract, by methods described in works devoted to analytical methods.

Meconium—the contents of the lower intestine of the fœtus at birth—is dark brown or green in color, almost odorless, acid in

reaction, and semi-solid in consistency. It contains epithelial cells, frequently stained green, fat globules, crystals of cholesterol and of bilirubin. In chemical composition it consists of about 80% water and 20% solids. The solids consist of mucin, biliary acids and pigments, cholesterol, fat, soaps, peptones, leucin, tyrosin and salts, notably calcium and magnesium phosphates. Stains produced by meconium may be distinguished from fæcal stains by the fact that the former give Gmelin's and Pettenkofer's reactions, while the latter do not.

Intestinal Concretions. — Besides gall-stones, the intestine may contain true intestinal concretions, which are, however, of much rarer occurrence in the human subject than in the lower animals. They usually consist of concentric layers of calcium carbonate or of tricalcic phosphate, with a little fat and pigment, deposited upon some insoluble foreign substance as a nucleus, or they may be formed in the vermiform appendix without a nucleus. The intestines of horses and cattle frequently contain large calcic calculi, sometimes weighing several pounds (16 lbs. in a horse); or "hair-balls," consisting of masses of hair agglutinated into hard balls. **Bezoar stones** are concretions from the intestines of certain goats and antelopes, which contain either **lithofellic acid**, a peculiar acid related to cholic acid, or **ellagic acid**, a derivative of gallic acid, and biliary pigments. **Ambergris** is an intestinal concretion of the whale, containing a non-nitrogenized substance, **ambraïn**, related to cholesterol.

THE BLOOD.

The blood being the circulating medium by which oxygen and the products of digestion are carried to the tissues, and by which the waste products of tissue metabolism are carried to the excretory organs, varies notably in composition in different parts of the circulation at different times and under varying conditions of health or disease.

The living, circulating blood consists of two parts, the **plasma**, the liquid portion, and the **corpuscular elements** suspended therein. It is desirable to consider the chemistry of these two constituents of the blood first, and subsequently that of the blood as a whole.

The blood, very soon after being removed from the living animal, undergoes the chemical and physical change of **coagulation**, involving modification of the proteins of the plasma, and the separation of the blood into the two new divisions of **clot**, consisting of the newly-formed fibrin and the corpuscles; and the **serum**, containing those constituents of the plasma not concerned in the formation of fibrin. In order, therefore, to obtain the plasma and corpuscles free from

each other some method must be adopted to prevent the occurrence of coagulation during the separation. Several methods have been used for this purpose :

(1) By taking advantage of the fact that the blood of the horse coagulates very slowly at low temperatures. Horse's blood is collected in a tall, narrow glass vessel, surrounded by a freezing mixture of ice and salt, which is then maintained at 0° until the corpuscles have settled. Coagulation does not take place for several days.

(2) On a small scale the corpuscles may be separated from the plasma by increasing the rapidity of their deposition by the use of the hæmatocrit. This is simply a centrifuge revolving with great rapidity (3,000 to 5,000 revolutions a minute). With the very narrow tubes used, the separation is complete in about two minutes, and before coagulation has interfered.

(3) The centrifuge, revolved at a lower speed, may be also used with larger quantities of blood, but then some agency must be used to delay coagulation. One method consists in injecting a solution of albumose into the circulation of a dog, collecting the blood and centrifugating it. The plasma so obtained is known as **peptone-plasma**. Or an infusion of the mouth of the leech may be similarly used.

(4) If the blood, as it flows from the vessel be mixed with either an equal volume of saturated solution of sodium sulfate, or with the same quantity of a 10% sodium chlorid solution, or with one-third its volume of a saturated solution of magnesium sulfate, and the mixture maintained at a low temperature, coagulation will be delayed sufficiently to permit the corpuscles to settle. This plasma is called **salt plasma**.

(5) The best method depends upon the removal of the calcium salts, whose presence is necessary to coagulation, by precipitation as calcium oxalate. The blood is received in a dilute solution of potassium oxalate in such proportion that the mixture contains 0.1% of oxalic acid, and the mixture set aside until the corpuscles deposit. The plasma, known as **oxalate plasma**, regains its power of coagulation on restoration of the calcium salts.

PLASMA AND SERUM.

The plasma, at the temperature of 0° , above which it rapidly coagulates into clot and serum, is a viscid liquid, yellowish, or greenish-yellow in color, strongly alkaline in reaction.

Composition.—But few complete analyses of blood-plasma have been made. Indeed, considering the variations in its quantitative composition, above referred to, the results of such analyses can only

be considered as applying to the particular sample analyzed, and not as representing the mean composition of the plasma except in a general way. The following are results obtained from horse's blood, the first an analysis by Hoppe-Seyler, the latter the mean of three analyses by Hammarsten :

	I.	II.
Water	908.4 . . .	917.6
Solids	91.6 . . .	82.4
Protein bodies	77.6 . . .	69.5
Fibrinogen	10.1 . . .	6.5
Serum globulin	67.5 {	38.4
Serum albumin		24.6
Fat	1.2	12.9
Extractives	4.0	
Soluble salts	6.4	
Insoluble salts.	1.7	

Fibrinogen, the parent substance of fibrin, exists in the plasma, chyle, lymph, and in transudates and exudates. It has the characteristic property of coagulating in presence of calcium salts and an enzyme (thrombin), with formation of fibrin. When moist, it forms viscid, elastic masses or flocks, which readily fuse together. It has the general properties of the globulins, from which it differs in that the addition of calcium chlorid solution to its very faintly alkaline and salt-free solution causes a precipitate which contains calcium, and soon becomes insoluble. This precipitate is not formed in presence of sodium chlorid, nor with an excess of calcium chlorid. Fibrinogen is insoluble in pure water, soluble in dilute sodium chlorid solution, and this solution, neutral, or very faintly alkaline, coagulates at 56° , apparently suffering decomposition into two globulins, the second of which coagulates at 65° . From its salt solution it is precipitated by dialysis. Its solutions are precipitated by addition of an equal volume of saturated sodium chlorid solution, and, completely, by excess of the solid salt; in which latter respect it differs from serum-globulin. It is also precipitated by passing a stream of CO_2 through its solution. It decomposes hydrogen peroxid energetically. Its solutions are lævogyrous, $[\alpha]_D = -52.2^{\circ}$. It is obtained from salt- or oxalate-plasma by precipitation with an equal volume of saturated salt solution and purification.

Fibrin is the substance formed in the so-called spontaneous coagulation of blood, lymph, and transudates, or by the addition of serum, or of thrombin, to a solution of fibrinogen. The typical fibrin, as obtained by whipping blood with a bundle of twigs or broom, and washing until white, is in elastic fibers, insoluble in water, alcohol, or ether. In dilute salt solution, putrefaction being

prevented, it dissolves very slowly at the ordinary temperature, somewhat more rapidly at 40° . In solution of HCl, KHO, or NaHO of 1 p/m it swells, gelatinizes, and slowly dissolves after some days. It decomposes hydrogen peroxid energetically, but not after having been heated, or in contact with alcohol.

A solution of pure fibrinogen does not coagulate at the ordinary temperature, but it does so very soon after addition of a little blood-serum, or of a fragment of fibrin washed with water only. These therefore contain a substance, an enzyme, called **thrombin**, or **fibrin-ferment**, which sets up the conversion of fibrinogen into fibrin. This substance is by some believed to be a globulin, by others a nucleoproteid. It is active in very small amount, most active at about 40° and in presence of calcium salts. It does not act in the absence of neutral salts, and its power is completely destroyed by a temperature of 70° . In the formation of fibrin the fibrinogen is considered to be split by the enzyme into fibrin and a soluble globulin, called **fibrinoglobulin**, which remains in the serum. The coagulation of blood is, however, a more complex process than the coagulation of fibrinogen alone, and in it the corpuscles play a part (see p. 667). The plasma does not contain thrombin, but its zymogen, **prothrombin**, which is converted into thrombin by the soluble calcium salts. Thrombin in solution when injected into the circulation causes death from thrombosis almost immediately.

Serum-globulin — Paraglobulin — Fibrinoplastic substance — occurs in the blood-plasma and serum, and in the red and white blood-corpuscles, and constitutes more than half of the total proteins of the blood, also in lymph, in transudates and exudates, and pathologically in the urine. It is not a simple substance, but a mixture of two or more globulins. It has the general properties of the globulins. When moist it forms white flocks, not elastic or sticky. It differs from fibrinogen in not being precipitated by an equal volume of saturated sodium chlorid solution, and only incompletely by salting with sodium chlorid to saturation. It is completely precipitated by saturation with magnesium sulfate, or by addition of an equal volume of saturated ammonium sulfate solution. Its coagulation temperature in solutions containing 5 to 10 per cent of sodium chlorid is 75° . Its solutions are lævogyrous, $[\alpha]_D = -47.8^{\circ}$. Serum-globulin, as usually obtained from blood, when boiled with dilute acids, yields a reducing substance. **Euglobulin** and **pseudoglobulin** are two components of the mixture called serum globulin. The precipitation limits of the former with ammonium sulfate are 2.8 and 3.4; those of the latter, 3.6 and 4.4. The former is precipitated by dialysis of its salt solutions, and is therefore insoluble in water; the latter is not so precipitated. But apparently these substances are themselves mixtures,

each being separable into a water-soluble component and one which is insoluble in water. The latter are called **para-euglobulin** and **para-pseudoglobulin**.

Serum-globulin is obtained from blood-serum by slight acidulation with acetic acid, and addition of from 10 to 20 volumes of water, or by passage of CO_2 through its dilute solution, when it separates as a flocculent precipitate, which is purified by solution in dilute salt solution, and reprecipitation by water. As so obtained it is not free from lecithins and thrombin. It can be obtained free from the latter from the fluid of hydrocele.

Serum-albumin—occurs in blood-plasma and serum, in lymph, in transudates and exudates, probably in many tissues, and, pathologically, in the urine. When moist it is a white, flocculent material; when dry, translucent, gummy, brittle, and hygroscopic. It has the general properties of the albumins. It is not a simple substance, but a mixture of three **serines**, of which one is amorphous and two crystalline, one crystallizing in hexagonal prisms, the other in long needles. The mixed serum-albumin has a coagulation temperature varying from 70° to 85° , depending upon the quantity of NaCl present, and the reaction. It is lævogyrous, $[\alpha]_D = -62.6^\circ$ to 64.6° . It has not been obtained entirely free from salts. From solutions containing the minimum amount of salts it is not coagulated by heat, or by alcohol, but is after addition of NaCl . Serum-albumin is distinctly basic, being capable of removing sulfuric acid from sulfates and forming a compound from which the acid cannot be washed out by water.

Blood-serum.—When blood is drawn from the blood-vessels it soon coagulates into a jelly-like mass, occupying the volume of the original liquid. This mass soon contracts and expels a liquid, which is the **serum**, and which differs from the plasma in that it contains thrombin, fibrinoglobulin, derived from fibrinogen, and **cell-globulin**, a protein derived from the leucocytes during coagulation, and has lost fibrinogen, fibrin and some portion of its salts, particularly of those of calcium. In other respects the two are qualitatively alike. It is a sticky liquid, more strongly alkaline than the plasma, sp. gr. 1027 to 1032, pale yellow, with a greenish tinge, usually clear, but opalescent or milky during digestion of fats.

The constituents of the plasma and of the serum, other than the proteins, being identical, are most readily studied in the serum, which is more easily obtainable than the plasma. They include the fats, carbohydrates, extractives and mineral salts. The term "extractives," in an analytical statement, is the equivalent of "miscellaneous" in a classification, and the substances arranged under this head are of diverse nature, present in small quantity, and, while they

are not separately determined in the particular analysis referred to, some of them are of great physiological interest.

Fats—exist in the plasma or serum, suspended in minute oil globules, as a fine emulsion. They are present during fasting in the proportion of 1 to 7 p/m, and are greatly increased in amount during digestion of fats. Soaps, derived from the fats, are also present. Besides the true fats (p. 366), the plasma contains lecithins (p. 367), cholesterol and cholesterol esters (p. 638).

Carbohydrates.—The carbohydrates of the blood appear to exist almost exclusively in the plasma, none having been found in the corpuscles, except glycogen in the leucocytes. They consist of glucose, glycogen, and a carbohydrate in some form of nitrogenized or phosphorized combination. Glucose is a constant constituent of the plasma, even during starvation, and is present in about the proportion of 0.5 to 1 p/m, without any notable variation in different parts of the circulation under normal conditions, except that it is greatly increased in amount in the portal blood during digestion of carbohydrates. When the proportion of sugar in the blood exceeds 3 p/m (hyperglykæmia), either from excessive absorption or in natural or experimental diabetes, it is eliminated by the urine (glycosuria). The amount of reducing substance, calculated as glucose, in the blood is increased after hemorrhages, and in diabetes, in which latter condition it may reach 9 p/m. Glycogen, although more usually a constituent of tissue elements than of the liquids of the body, is present in the plasma in very variable amount, usually in mere traces. The plasma contains small quantities of a substance other than glycogen, and containing nitrogen and phosphorus, which does not itself reduce Fehling's solution, but which on hydrolysis by dilute acids yields a reducing substance. The nature of this substance, which also occurs in the liver, and has been called **jecorin**, is undetermined, although it is certain that it is not a chemical individual, as on fractional precipitation it gives products in which the phosphorus varies from 3.16 to 0.38 per cent, and the nitrogen from 4.55 to 1.45. The so-called **animal gum**, obtained from the serum, also yields a reducing substance by the action of dilute acids, does not ferment, is optically inactive, and is said to have the empirical formula $(C_6H_{10}O_5)_n$. Still another reducing substance, which is difficultly fermentable, is soluble in ether, and probably consists of conjugate glucuronates, exists in small quantity in the plasma.

Enzymes.—The plasma contains several enzymes or zymogens, which are probably produced in whole or in part by the corpuscular elements: (1) **Prothrombin**, the zymogen of thrombin, the fibrin forming enzyme (p. 668); (2) a diastatic enzyme, or **amylase**. Blood serum or lymph, added to starch paste or glycogen solution,

brings about the formation of maltose and isomaltose, if the mixture be kept at about 40° ; (3) an invertin, a maltase, which brings about the hydrolysis of the product of the diastatic action, with formation of glucose, if the action above mentioned be allowed to continue; (4) a glucase (an oxidase, not an invertin). The proportion of glucose in blood serum gradually diminishes on standing, even in the absence of organized ferments. This glucolysis is due to the action of an enzyme whose activity is destroyed by a temperature of 54° , and which apparently originates in the leucocytes; (5) a lipase, which saponifies neutral fats. Besides the above the blood contains substances, possibly enzymes, which bring about the conversion of the emulsified fats into some unknown form of soluble combination, and which arrest the action of the digestive enzymes absorbed from the intestine.

Extractives.—The most abundant are urea, creatin, and salts of uric, carbamic, phosphocarnic, paralactic and hippuric acids, etc.; also, pathologically, xanthin bases, leucin, tyrosin, acetone, and biliary salts and pigments. Urea is present in human blood in the proportion of 0.14 to 0.4 p/m; more abundant in the blood of the splenic, portal and hepatic veins than in that of the carotid artery; more abundant in placental blood, 0.28 to 0.62 p/m. In animals the proportion rapidly increases after nephrectomy, reaching 2.06 to 2.76 p/m in 27 hours. In human blood the amount is greatly increased in cholera, 2.4 to 3.6 p/m, and, particularly, in nephritis, 15.0 p/m.

The yellow coloring matter of the plasma and serum appears to belong to the class of luteïns, or lipochroms, which exist in fats, corpora lutea, egg-yolks, etc. A coloring-matter has been obtained from the serum of ox blood, which, in amylic alcohol solution, gives a spectrum of two bands, one covering F, the other between F and G.

Mineral Salts.—The serum contains a somewhat smaller quantity of mineral material than the plasma, a part of the calcium salts having passed into the clot. The total ash of the serum equals 8.3 to 9.2 p/m. In composition it does not vary greatly in different animals. In 1000 parts of human blood serum there are: K_2O —0.387 to 0.401, Na_2O —4.290, CaO —0.155, MgO —0.101, Cl —3.565 to 3.659, besides phosphoric acid, and traces of silicon, fluorin, iron, manganese, copper and ammoniacal compounds. The most abundant constituent of the ash is sodium chlorid, 60 to 70 per cent. of the ash. The calcium and magnesium are probably present as phosphates, and the former also as chlorid, the sodium and potassium as chlorids, phosphates and carbonates or bicarbonates. The amount of base present is in excess of the amount of acid, therefore a part of the bases must be present as carbonates or in organic combination.

The presence of carbonates is demonstrated. The organic acids above mentioned are contained in the plasma in saline combination; and the existence of mineral elements in protein combination is shown by the fact that the mineral constituents are not completely removable by dialysis.

BLOOD CORPUSCLES.

The corpuscular elements of the blood are of three kinds: the **red corpuscles**, the **white corpuscles**, or **leucocytes**, and the **plaques**, or **platelets**.

The **red corpuscles** are separated from the plasma by the methods given above. As they are heavier, they sink more rapidly than the other corpuscular elements, and are consequently found in the lower part of the deposit. When they are required in larger quantities, the blood is defibrinated by whipping, diluted with ten volumes of 1 per cent NaCl solution, filtered through muslin, and centrifuged. The corpuscles are repeatedly washed with salt solution in the centrifuge, and freed from fats, lecithins and cholesterol by washing with warm alcohol-ether on a paper filter.

The number of red corpuscles in normal blood is fairly constant at 5,000,000 to 5,500,000 in a cubic millimeter in the male, and 4,500,000 in the female. Pathologically, the count may rise to 6,500,000, with loss of large quantities of water from the system, or fall as low as 500,000 in pernicious anæmia. Their variations in size, shape and number have been the subject of much careful study. Suffice it to say here that in man they are rounded bi-concave discs, non-nucleated, having an average diameter of 7 to 8 μ (μ =micro-millimeter=0.001 mm.). In other mammals, except camels, they have the same shape as in man, but differ in size, while in camels, birds, fishes and reptiles, they are oval and nucleated.

On contact with water the corpuscles swell and give up their coloring matter, which goes into solution, leaving the **stroma**, a colorless mass, which may be made to retract to the original size and shape of the corpuscle by the action of carbon dioxid, dilute acids, acid salts, and other agents. By the action of water or of very dilute salt solutions, or by alternate freezing and thawing, or by agitation with chloroform or ether, or by the action of bile, the corpuscles undergo **cytolysis**, also referred to as **hæmolysis**, **hæmocytolysis**, or **erythrolysis**, i. e., they are broken down and their coloring matter goes into solution, a change which is referred to when thus produced outside the body as **lakeing**, or **lake-coloring** (lakfarben), from the resemblance of the product to the pigments called "lakes." Cytolysis also occurs normally in the body to a certain extent, cells which have

outgrown their usefulness being disintegrated, and the liberated coloring matter split in the liver for the formation of bile pigment from the non-ferruginous part, while the iron is in all probability utilized for the production of new blood coloring matter. In disease, notably in so-called hæmato-hepatogenous jaundice and in acute febrile diseases, by the action of the **cytotoxins**, or **cytolysins** existing in certain sera (p. 671), and by the action of many venoms and poisons, such as rattlesnake and cobra venoms, hydrogen arsenid, chlorates, abrin, saponin, etc., the destruction of red corpuscles is increased, sometimes enormously.

If portions of defibrinated ox-blood, or of the corpuscles therefrom, be agitated with solutions of NaCl of varying degrees of concentration, the lowest being, say, 0.2 per cent and the highest 0.7 per cent, it will be found that lakeing will occur, and the solution will become colored from dissolved hæmoglobin, in all solutions having a less degree of concentration than 0.585 per cent, but not in the others. If, in place of solutions of NaCl, we use solutions of KNO_3 , it will be found that the lowest concentration in which lakeing will not occur is 1.01 per cent. That lowest degree of concentration of a solution of a given salt in which lakeing does not occur is called the **isotonic coefficient** of that salt, as 0.585 for NaCl and 1.01 for KNO_3 , and solutions of that degree of concentration are said to be **isotonic** with the corpuscles, while solutions of greater concentration are said to be **hyperisotonic**.

Solutions of NaCl and of KNO_3 of 0.585 and 1.01 per cent respectively are N/10 solutions of those salts, and experiments with solutions of other salts have shown that with them N/10 solutions are also isotonic. Such solutions, containing equal numbers of molecules, are isosmotic with each other (p. 67), and it may be considered as demonstrated that the phenomenon of lakeing is due to difference of osmotic pressures in the corpuscles and in the surrounding medium, although the purely physical act of diffusion is accompanied by one of chemical nature involved in the liberation of the coloring matter from the condition of combination in which it exists in the corpuscles (below). The plasma is, however, hyperisotonic. Its osmotic pressure, as determined by its freezing point (pp. 67-69), is equal to that of a solution of NaCl of 0.9 per cent concentration, and the difference between the condition of equality of osmotic pressures and that represented by the isotonic coefficient, about 2.3 atm., may be considered as representing the degree of pressure required to rupture the corpuscles and cause lakeing. Usually solutions isosmotic with 0.58 per cent NaCl solution are also isotonic, but certain substances, such as urea, ammonium salts, glycerol, sodium carbonate, and the poisons above mentioned, are exceptions to the rule, and lakeing

occurs in their stronger solutions. Apparently this departure from the rule depends upon an action upon the stroma, as it is not observed with saponin after the stroma has been hardened by formic aldehyde, and has had its cholesterol and lecithins removed by ether.

The freezing point of normal blood is fairly constant at -0.56° . This depression from $0^{\circ}=\Delta=-0.56^{\circ}$, represents an osmotic pressure of 6.78 atm. (p. 68). This pressure is the sum of the pressures of all of the molecules and ions, mineral and organic, present in the blood, and, as that fraction due to fibrin is small, the osmotic pressures of the whole blood and of the plasma and serum are nearly alike. With dilution of the blood, as by absorption of large quantities of water, the value of Δ may normally fall to $-0.51^{\circ}=6.17$ atm., and with concentration, as by absorption of notable quantities of solids, particularly of highly ionized molecules such as salts, it may rise to $-0.62^{\circ}=7.5$ atm. Concentration may also result from deficient elimination of solids because of renal disease, when the value of Δ may exceed $-1^{\circ}=12.1$ atm. The determination of the value of Δ in the blood, particularly when taken in connection with the same value for the urine from each kidney separately, is therefore of service in the diagnosis of kidney disease.

The electrical conductivity of blood serum depends upon the concentration of the ions present, and is not affected by unionized molecules (pp. 41, 75). It is therefore influenced by the quantity of salts, but not by the proteins, urea, or other non-conductors, and is an index of that fraction of the blood-concentration, shown by the osmotic pressure, which is due to salts. The value of κ for a column of serum 1 sq. cm. in cross section and 1 cm. long is $\kappa=0.012$. As each salt contributes to the conductivity in proportion to its concentration, a large fraction of κ is due to NaCl. Variations in the quantity of salts in the plasma or serum can be better studied by variations in the value of κ than by analyses, because the determinations are more delicate, and because the ash, which is the material examined in analyses, contains constituents produced by combustion of organic substances, which are not present in the original liquid.

Composition.—Analyses of human blood corpuscles show them to contain 681.63 to 687.86 p/m of water, and 318.37 to 312.14 of solids. The corpuscles of animals contain a larger proportion of solids. In the solids the proportion of organic constituents to mineral salts is much greater in the corpuscles than in the plasma. The 318.37 and 312.14 p/m of solids in the above analyses contain respectively 311.1 and 303.17 of organic constituents and 7.36 and 8.97 of mineral. The solids consist of a proteid coloring matter, containing iron, hæmoglobin; albumins, including a nucleoalbumin and a globulin; lecithins, cholesterol, fatty acids, and salts.

Blood Coloring Substances.—The red color of the blood depends upon the presence in the red corpuscles of a coloring matter, **hæmoglobin**, which exists in the two forms of **hæmoglobin** and **oxyhæmoglobin**. In what condition this pigment exists in the corpuscles is not clearly established. That it exists in some form of combination may be inferred from the facts that in the corpuscles it is insoluble in water, while free hæmoglobin, that of many animals at all events, is readily soluble; that hæmoglobin is crystalline, while no crystalline structure can be made out in the corpuscles; that the oxy-compound in the corpuscles gives off its oxygen in a vacuum more readily than ordinary oxyhæmoglobin does; that the pigment in the corpuscles decomposes hydrogen peroxid without itself suffering oxidation, which is not the case with hæmoglobin; and that the native substance is more resistant to the action of reagents than free hæmoglobin. It certainly exists in the corpuscles in two forms of oxidation, one yielding hæmoglobin, and largely predominating in the blood in asphyxia, the other yielding oxyhæmoglobin, and largely predominating in arterial blood; the proportion of the two in venous blood being intermediate between the above. To the former of these combinations the name **phlebin** has been given, to the latter the name **arterin**.

Hæmoglobin—**Reduced Hæmoglobin**—exists in very small amount in arterial blood, and almost exclusively in the blood after death from asphyxia. It is more soluble and more difficultly crystallizable than oxyhæmoglobin, but isomorphous with it, although the crystals are darker in color. Its aqueous solution is purple, and gives a spectrum of a single broad band, covering D, and about three-fourths of the space between D and E. The violet end of the spectrum is less absorbed than with oxyhæmoglobin solutions of corresponding concentration (No. 1, Fig. 43, p. 661). It absorbs oxygen rapidly from air, with formation of oxyhæmoglobin. Hæmoglobin is obtained from oxyhæmoglobin by bringing its solution into a vacuum, by passing indifferent gases through it, or by the action of reducing agents, such as Stokes' reducing reagent, consisting of an ammoniacal solution of ferrous tartrate.

Oxyhæmoglobin—is the form in which the blood-coloring matter is usually obtained. The hæmoglobins from the blood of different animals differ from each other in several particulars; in crystalline form, in solubility, and in chemical composition. The most usual crystalline form, including that of human hæmoglobin, is in rhombic prisms or needles, but hæmoglobin from guinea pig's blood crystallizes in rhombic octahedra, and that from the squirrel in hexagonal plates. They differ also in the facility with which the crystals are formed, which is inversely as their solubilities. The hæmoglobin of

the blood of the horse and guinea-pig are sparingly soluble and crystallize easily, those of human blood, ox blood and pig's blood are very soluble, and crystallize with difficulty. The crystals of oxyhæmoglobin are bright-red in color, and are doubly refracting. They contain from 3 to 10% of water of crystallization. In some hæmoglobins there are two atoms of sulfur to each atom of iron, in others there are three. The hæmoglobins of most animals contain carbon, hydrogen, nitrogen, iron, sulfur, and oxygen; but those of certain birds also contain phosphorus, probably as an admixture in the form of a nucleic acid derived from the nuclei. The molecular weight of hæmoglobin is certainly very large; a formula for that from dog's blood has been given as $C_{636}H_{1025}N_{164}FeS_3O_{181}$, corresponding to a molecular weight of 14,129; which must, however, be accepted with some reserve. Oxyhæmoglobin is more readily soluble in dilute acids and alkalies than in pure water, insoluble in alcohol, ether, chloroform, benzene, or carbon disulfid. When dried in vacuo at the ordinary temperature, it may be heated to 115° without suffering decomposition.

When hæmoglobin from the blood of the ox absorbs oxygen to form oxyhæmoglobin, it does so in the proportion of 1.34 cc. of oxygen for each gram of hæmoglobin (at 0° and 760 mm.), which, calculated for weight, is equal to five atoms of oxygen for three molecules of hæmoglobin. The combination is a "loose" one, in that the combined gas is readily given off in a vacuum, or by passage of an indifferent gas through the solution. Hæmoglobins are proteids, and when heated in solution to 60° to 70° , or when acted upon by acids, alkalies, or certain metallic salts, are decomposed into a protein and a colored derivative containing iron. The protein, called **globin**, is a histon, insoluble in water, but very soluble in dilute acids or alkalies, insoluble in ammonia in presence of ammonium chlorid. It is coagulated by heat, but the coagulum is soluble in acids. Nitric acid precipitates it in the cold, but not from warm solutions. The ferruginous pigment resulting from the decomposition differs according to the degree of oxidation of the hæmoglobin. If oxygen be excluded, the product is **hæmochromogen**, but in presence of oxygen, **hæmatin** (p. 663) is formed. The proportions of globin and of coloring matter obtained from hæmoglobin have been 94 per cent of the former and 4.3 per cent of the latter.

The spectrum of oxyhæmoglobin varies with the degree of concentration of the solution. When a solution, sufficiently concentrated to be opaque when observed spectroscopically in a layer of a given thickness, is gradually diluted, it first allows portions of the red and orange to pass. On further dilution, light appears in the green, leaving a single broad band extending from about midway between C and D to beyond b (No. 2, Fig. 43). On still further dilution this band divides

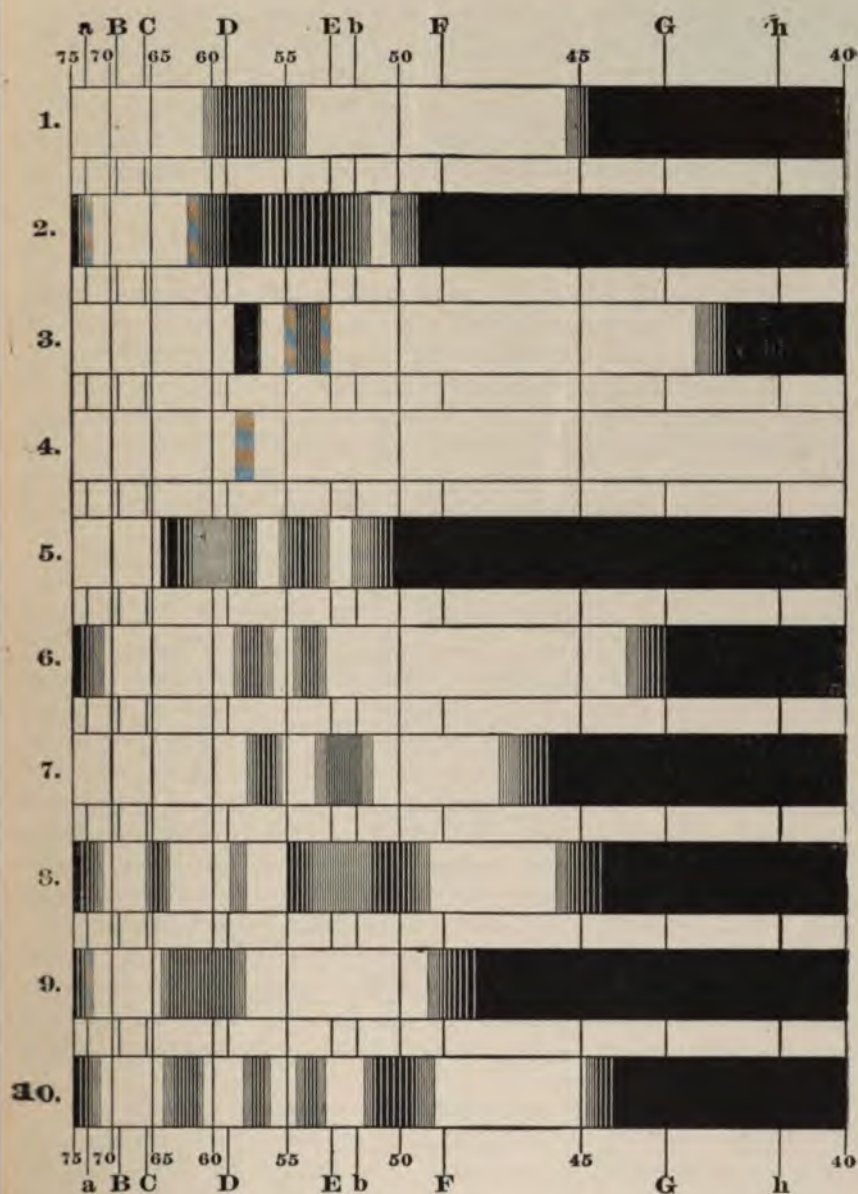


FIG. 43. Spectra of : (1) Reduced hæmoglobin; (2) Oxyhæmoglobin, concentrated; (3) Same, dilute; (4) Same, very dilute; (5) Methæmoglobin, in faintly alkaline solution; (6) Carbon monoxid hæmoglobin; (7) Hæmochromogen, in alkaline solution; (8) Hæmatin, in acid solution; (9) Hæmatin, in alkaline solution; (10) Hæmatoporphyrin, in acid solution.

into two, giving the characteristic oxyhæmoglobin spectrum, consisting of two bands, one (α) between D and E, and resting on D, the other (β) extending from about midway between D and b to b. The band α is narrower, darker and more sharply defined than β (No. 3, Fig. 43). This spectrum is still visible with a solution of 0.1 p/m in a layer 1 cm. thick. With further dilution the band β disappears first (No. 4, Fig. 43). On addition of reducing agents the spectrum changes to that of hæmoglobin (No. 1, Fig. 43).

Pseudohæmoglobin.—When a solution of oxyhæmoglobin is reduced by ammonium sulphid until it gives the spectrum of hæmoglobin, it will still give off oxygen in the vacuum. In this condition it is, therefore, not completely reduced, and the intermediate form of oxidation which is supposed to exist in the solution has been called pseudohæmoglobin.

Methæmoglobin—is a product of oxidation of hæmoglobin, containing the same proportion of oxygen as oxyhæmoglobin, but in a state of firmer chemical union, which may be expressed by writing

the formula of oxyhæmoglobin as $\text{Hb} \begin{smallmatrix} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{smallmatrix}$, and that of methæmo-

globin as $\text{Hb} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$. Methæmoglobin occurs in transudates and exudates, and in the urine in hæmaturia and hæmoglobinuria, and, particularly, in poisoning by poisons such as potassium chlorate, amyl nitrite and the alkaline nitrites. It is formed from hæmoglobins when blood is kept in hermetically sealed vessels, or by the action upon them of many oxidizing agents, ozone, permanganates, chlorates, nitrites, etc., or of certain reducing agents such as hydrogen and the di- and triphenols. It crystallizes in red-brown, hexagonal prisms, needles or plates, which form a brown-red solution with water, which changes to bright-red with alkalies. It is very soluble in water. Its neutral, or faintly alkaline or acid, solutions give a spectrum of a single band between C and D, nearer to C and united by a space of partial absorption with the α band of the oxyhæmoglobin spectrum, which is usually also present (No. 5, Fig. 43). By the action of reducing agents upon faintly alkaline solutions the spectrum changes to that of reduced hæmoglobin.

Carbon Monoxid Hæmoglobin—is a form of combination of hæmoglobin existing in the blood of those poisoned by carbon monoxid, or by illuminating gas, and whose production is the cause of death by that poison. It is a definite compound, containing one molecule of CO for each molecule of hæmoglobin, and, being more stable than oxyhæmoglobin, is not oxidized in the lungs, and thus destroys the oxygen-carrying function of the blood coloring-matter, but if oxygen be present in great excess the influence of mass-action is

exerted and oxyhæmoglobin is slowly regenerated. It is formed by passing CO through blood, or through a solution of hæmoglobin or of oxyhæmoglobin. It crystallizes readily in forms isomorphous with oxyhæmoglobin, but more bluish in color, more stable, and less soluble. Its solutions are bright-red in color and give a spectrum of two bands, resembling that of oxyhæmoglobin, but differing therefrom in that the two bands are of equal intensity, are somewhat differently placed (No. 6, Fig. 43), and also in that reducing agents do not change the spectrum to that of reduced hæmoglobin. Carbon monoxid blood, when mixed with an equal volume of NaHO solution (sp. gr. 1.3) forms a bright-red mass, while normal blood, similarly treated, forms a dirty-brown mass with a greenish tinge.

Carbon Dioxid Hæmoglobin.—A solution of hæmoglobin shaken with a mixture of oxygen and carbon dioxid takes up both gases, forming molecular combinations with each. It is supposed that the carbon dioxid combines with the protein component of the coloring matter. Carbon dioxid alone is also absorbed by hæmoglobin solutions, and the spectrum is then that of reduced hæmoglobin, while a part of the coloring matter is decomposed with separation of globin.

Hæmochromogen—is formed by the action of NaHO upon hæmoglobin in complete absence of oxygen, or by the action of reducing agents upon hæmatin in alkaline solution. It is soluble in alkalies with a cherry-red color, and such solutions give a spectrum of two bands, resembling the oxyhæmoglobin bands in relative intensity, but placed nearer to the violet end of the spectrum (No. 7, Fig. 43).

Hæmatin—is produced by decomposition of oxyhæmoglobin by alkalies, by dilute acids, or by mere heating to 80° . Or it may be obtained by decomposition of hæmin crystals by NaHO, and precipitation by dilute HCl. It exists in old transudates, is formed by peptic or tryptic digestion of hæmoglobin, and is met with in the urine in poisoning by hydrogen arsenid. It is amorphous, blue-black, insoluble in water, dilute acids, alcohol, ether, or chloroform; sparingly soluble in hot glacial acetic acid with formation of hæmin; soluble in acidulated alcohol or ether, very soluble in dilute alkalies. Its alkaline solutions are dichroïc, red by reflected light, green by transmitted; its acid solutions are brown. In acid solution in alcohol or ether it gives a spectrum of four bands (No. 8, Fig. 43): α , the darkest, near to C, and extending about one-third to D; β resting on D, narrower and paler than α ; γ between D and E, nearer to E, broader and paler than α ; δ the broadest of the four, a pale band whose center is midway between b and F, and covering about three-quarters of the space. The interval between γ and δ is partly absorbed. In alkaline solution hæmatin gives a spectrum of a single band, extending from near C to beyond D (No. 9, Fig. 43).

The empirical formula of hæmatin is $C_{32}H_{32}N_4FeO_4$. When heated dry it gives off pyrrole. By oxidation with potassium chromate in glacial acetic acid solution it yields a monobasic imid-acid, called hæmatinic acid, $\begin{array}{c} CH_3.C.CO \\ \parallel \\ HOOC.CH_2.CH_2.C.CO \end{array} > NH$, which by saponification with MgO yields the anhydrid, $HOOC.C_5H_7 < \begin{array}{c} CO \\ CO \end{array} > O$, of the parent tribasic acid, $HOOC.C_5H_7 < \begin{array}{c} COOH \\ COOH \end{array}$, which acids are themselves derivatives of hæmopyrrole, or methylpropylpyrrole (p. 510). The same acids, or their isomeres, are similarly obtained from hæmatoporphyrin, bilirubin, and urobilin. Hæmatin dissolves in concentrated H_2SO_4 , losing its iron, and the product by hydration is converted into hæmatoporphyrin.

Hæmin—is a compound of hæmatin with chlorin or iodin, whose formation is utilized as the most characteristic test for blood. It forms red-brown crystals, which, when perfect, are rhombic prisms, insoluble in water, alcohol, ether, dilute acids or chloroform, soluble without decomposition in hot glacial acetic acid, soluble with decomposition in acidulated alcohol or in dilute NaHO solution. The crystals, known also as **Teichmann's crystals**, are best obtained as follows: a fragment of the dried stain is placed upon a glass slide, upon which a very minute drop of dilute sodium chlorid, or iodid, solution has been previously evaporated, and covered with a cover-glass. Glacial acetic acid is then run in beneath the cover, and the slide cautiously heated over a very small flame until bubbles just begin to appear, when the slide is raised about three inches above the flame and kept warm for a few minutes, while the loss of acid by evaporation is supplied by fresh glacial acetic acid placed at the edge of the cover with a slender glass rod. The slide is now allowed to cool, and, during cooling and evaporation of the acid, examined with a one-fifth inch objective. The crystals are usually found near the edge of the cover, or imprisoned in the remains of the clot, and are generally all in a small space, while the remainder of the preparation is free from them. The acid must not be allowed to boil, or the crystals may be mechanically carried out from under the cover. The formation of the crystals under these conditions may be accepted as certain evidence of the presence of blood-pigment, but their non-formation is not evidence of its absence. They cannot be obtained if the stain contains iron-rust, or has been treated with chlorin or with certain kinds of soap. In place of acetic acid and a chlorid, Stryzowski's reagent may be used to advantage, as it softens old stains more readily. It consists of a freshly prepared mixture of equal volumes of glacial acetic acid, alcohol, and water to which a drop or

two of hydriodic acid solution are added. Sometimes the crystals may be obtained even from stains on iron, by prolonging the contact with the acid or reagent.

Hæmin was formerly considered to be a simple chlorid (or iodid) of hæmatin. Its chlorin is, however, in combination with carbon or with iron, and may be almost completely removed by washing with hot water. Its molecule contains two hydroxyls, which are readily replaceable by alkyls or acidylys. As usually produced in the manner above described, the crystals are those of a monoacetyl ester, **acethæmatin**, $C_{32}H_{30}(C_2H_3O)O_3N_4ClFe$, corresponding to a hæmin of the composition $C_{30}H_{31}O_3N_4ClFe$. In this compound, however, the acetyl is not substituted in one of the hydroxyls, which are replaceable to form dialkyl derivatives in acethæmin as they are in hæmin.

Hæmatoporphyrin—is an isomere of bilirubin (pp. 637, 641), therefore containing no iron, $C_{32}H_{36}N_4O_6$, and is derived from hæmatin: $C_{32}H_{32}N_4FeO_4 + 2H_2O = C_{32}H_{36}N_4O_6 + Fe$. It occurs normally in urine in minute quantity, and is notably increased in poisoning by sulfonal. It forms a compound with HCl which crystallizes in long, red-brown needles, and is precipitated from its HCl solution by partial neutralization and addition of sodium acetate, as an amorphous, brown powder. It is soluble in dilute acids or alkalies, the acid solutions having a purple color, and the alkaline solutions being red. Reducing agents convert it into urobilin, and when injected into the circulation of rabbits it is partly eliminated in that form. In acid solution it gives a spectrum of two bands (No. 10, Fig. 43), β , the narrower and less intense, between C and D, nearer to D; and α , much darker and broader, about midway between D and E, with a space of less complete absorption extending nearly to D. In alkaline solution it gives a four-band spectrum, one (α) between C and D, a broader one (β) over D, a third (γ) between D and E, extending nearly to E, and a fourth (δ) between b and F. On addition of alkaline zinc chlorid solution the bands α and δ gradually fade out, leaving β and γ .

Hæmatoïdin—another decomposition-product of hæmoglobin, is identical with bilirubin (p. 637).

The solids of the **stroma** (p. 656) of mammalian corpuscles represent but a small fraction of their weight. The proteins are: a globulin, which is possibly identical with serum globulin, and a nuclealbumin. The nucleated cells of the birds and fishes contain a nucleoproteid, which forms a mucilaginous solution with a 10 per cent solution of NaCl, but the non-nucleated cells of the mammalia contain no similar substance. The proportion of non-proteid proteins to hæmoglobin is much greater in nucleated than in non-nucleated corpuscles. Thus human corpuscles contain in 1,000 parts 868 to 943 of

hæmoglobin against 122 to 51 parts of albumins, while in serpents' blood the proportion is 467 hæmoglobin to 525 of albumins. The red corpuscles of frogs' blood also appear to contain fibrinogen, or a related protein. Lecithins exist in human corpuscles, in the proportion of 3.5 to 7.2 p/m, and cholesterol to the amount of about 2.5 p/m. The total ash of human corpuscles, including the iron derived from the hæmoglobin and the phosphoric acid derived from the lecithins, constitute 3.5 to 3.7 p/m of their weight. The salts vary in different animals. In the corpuscles of the pig, ox, horse and dog the sodium compounds are notably more abundant than those of potassium, while human corpuscles contain sodium compounds equivalent to 0.24 to 0.65 Na_2O , and potassium compounds equivalent to 1.41 to 1.59 K_2O . The mineral salts present are potassium and sodium chlorids and phosphates, with mere traces of magnesium salts. Calcium compounds, so important in the serum, are entirely absent from the corpuscles.

The **leucocytes**, or **white corpuscles**, are rounded, colorless protoplasmic masses, endowed with the power of amœboid movement, having no limiting membrane, which, on addition of water or of 1% acetic acid, are seen to have from one to four nuclei, round or irregular in outline. They are less numerous than the red corpuscles, the average proportion between the two being from 1:350 to 1:500; but their number varies greatly under varying normal, as well as pathological, conditions. Histologically they are divided into several groups, the members of which differ from each other in size, in appearance, and in their behavior towards staining agents. Although no differences in chemical composition between these several kinds of white corpuscles are known to exist, the differences in their behavior towards stains, which are in reality chemical reagents, render it highly probable that they are not chemically identical. Indeed our knowledge of the chemical composition of the leucocytes is fragmentary. The different action of staining agents upon nuclei and protoplasm indicates differences in the nature of their constituents. The most abundant protein in the leucocytes is the nucleoproteid **nucleohiston** (p. 591), soluble in water and precipitated by acetic acid. Besides this they contain a mucin-like substance which swells to a mucilaginous mass on contact with alkalies, and is very similar to, if not identical with, the **hyaline substance of Rovida**, which exists in pus cells, and two cell-globulins, coagulating at 50° and 73° . The prothrombin (p. 668), which is furnished by the leucocytes, may be derived from one of these proteins. Glycogen, fat, cholesterol and lecithins are also present in small amount. The total phosphorus in the leucocytes is 3.01 per cent, and their total nitrogen 15.03 per cent.

Very little is known of the chemical composition of the **plaques** beyond the probability that they consist largely of albumins and nucleoproteins.

THE BLOOD AS A WHOLE.

The color of the blood is bright-red if arterial, bluish-red if venous, bright cherry-red in poisoning by carbon monoxid, brownish-red in poisoning by potassium chlorate, anilin, or nitro-benzene, dark purple-red after death from asphyxia. It is opaque, even in thin layers. It is salty in taste; and its odor is similar to that of the animal, being more pronounced after addition of H_2SO_4 ; sp. gr. 1045 to 1075. The reaction, which is alkaline, cannot be determined in the usual way, owing to the color of the blood. It is shown by allowing a few drops of blood to remain for about five minutes upon a slab of plaster of Paris which has been previously soaked in a neutral solution of azolitmin and dried, when, on washing off the blood, a blue stain remains. The alkalinity of the blood depends in part upon the presence of alkaline bicarbonates (p. 690) and phosphates, and in part upon alkaline protein compounds. The normal degree of alkalinity of human blood has been given by different observers as equal to from 3.38 to 5.95 p/m of sodium carbonate, or 2.55 to 4.5 p/m of sodium hydroxid. Usually the limits of normal variation are placed at 3.3 to 5.3 p/m Na_2CO_3 , or 2.5 to 4.0 p/m NaHO . The alkalinity of the blood rapidly diminishes after its removal from the circulation, by reason of the generation of acids, which has led to results lower than the above, some authors giving the normal limits as low as 1.8 to 3.0 p/m NaHO . Normally the degree of alkalinity is greater in men than in women and children; and is diminished after violent muscular activity. It increases with activity of the stomach digestion, and subsequently diminishes from absorption of hydrochloric acid and peptones from the intestine. Pathologically, it is diminished in anæmia, leukæmia, uræmia, diabetes, hepatic diseases, high fevers, and in acidism due to administration of mineral acids or to the generation of organic acids in the body. It is increased by administration of alkalies, by cold baths, and in phthisis, erysipelas, and septicæmia (p. 676).

The change of **coagulation**, which the blood undergoes shortly after being drawn from the blood-vessels, is a chemical phenomenon dependent upon physical conditions, the precise nature of which has not been satisfactorily explained. Coagulation takes place with different degrees of rapidity in the blood of different animals, and with different individuals of the same race. In human blood it usually begins in 2-3 minutes after the blood is drawn, and it results in the formation of a jelly-like mass in 7-8 minutes. If it take place

rapidly the clot is uniform in appearance, but if it be delayed the corpuscles sink, the red more rapidly than the white, and the upper part of the clot, the "buffy coat" or "crusta phlogistica," is pale in color, and contains few red corpuscles and many white ones. Coagulation is delayed by cold, diminished oxygen-content, increased carbon dioxid, the presence of acids, alkalies, ammoniacal salts, oxalates, fluorids, egg-albumin, sugar, dextrin, glycerol, albumoses, snake-poison, toxalbumins, or an infusion of the mouth of the leech, or by collection in oil. It is accelerated by warmth, contact with air, whipping, contact with solids to which it adheres, or addition of leucocytes, nucleoproteids, or extracts of lymphatic glands, testicles, or thymus.

As to the cause of coagulation, and particularly, its non-coagulation in the vessels during life, opinions differ. The following facts, in addition to others already discussed, bear upon the question: (1) the blood does not coagulate while in contact with living, healthy blood-vessels; (2) it remains fluid in a ligated section of a vein, removed from the body; (3) it coagulates rapidly when collected in a vacuum over mercury; (4) it does not coagulate when collected through an oiled or vaselined canula into a similarly prepared vessel; (5) in such vessels it does not coagulate when stirred with an oiled or vaselined glass rod; but, (6) it does coagulate when stirred with an unoiled rod; (7) under the conditions of 5 and 6, coagulation begins when a film of solid forms upon the surface by drying, or if a small quantity of dust be present in the oil or vaseline; (8) it coagulates in living blood-vessels when their internal surfaces become roughened, or in presence of foreign material with rough surfaces. From these facts it may be inferred that the change does not depend upon the presence of air, but that it does depend in some way upon the physical condition of adhesion, as the formation of crystals may be provoked in a strong solution of a salt by the addition of even a minute particle of dust, and that there exists in the blood a condition of unstable equilibrium comparable with that in supersaturated solutions.

As to the nature of the chemical changes involved in coagulation, opinions differ. It is universally admitted that the corpuscles, particularly the leucocytes and plaques, contain a zymogen, **prothrombin**, from which an enzyme, **thrombin**, is produced. It is also generally, though not universally, conceded that this enzyme causes coagulation by splitting fibrinogen into the insoluble fibrin and the soluble fibrinoglobulin; and that the continued existence of the enzyme in the circulating blood causes death by thrombosis. The presence of calcium salts is necessary to coagulation, as is shown by the prevention of such action by the removal of calcium by oxalates or other precipitants of that metal, and by the fact that oxalate plasma regains its

power of coagulation on restoration of calcium salts. As the separated fibrin contains a considerable amount of calcium, it has been suggested that during coagulation the calcium-containing thrombin gives up its calcium to fibrinogen, with the formation of fibrin, while prothrombin, which has a less calcium-content than thrombin, is regenerated, and may in turn regenerate thrombin by combination with calcium salts (Peckelharing). According to another explanation of the chemism of the process the leucocnuclein, or nucleic acid of the nucleohiston of the leucocytes, in the presence of calcium salts, decomposes fibrinogen with formation of an albumose-like substance (fibrinoglobulin) and a hypothetical substance, called **thrombosin**, which latter, combining with calcium, forms fibrin (Lillienfeld). This latter view, so far as concerns the activity of nucleohiston in the process, is supported by the fact that solutions of fibrinogen, not spontaneously coagulable, are coagulated on addition, not only of blood-serum, but also of cells, such as yeast, spermatozoa, etc., containing nucleoproteids. These views may be reconciled, with the exception of the supposed existence of thrombosin, upon the supposition that prothrombin and nucleohiston are identical either in kind or in action.

BLOOD SERUM AND BACTERIAL ACTION.

A brief notice of the bacteriological investigations of the propagation, inhibition and effects of bacterial life in blood serum, which have led to results of the greatest importance in pathology and in medicine, is of interest in this place in so far as such actions are probably chemical in their nature.

Immunity—Antitoxins.—We have seen (p. 572) that pathogenic bacteria produce, as endogenous poisons which are the agents causing the manifestations of disease, substances called **toxins**, which are in all probability chemical individuals, although nothing is as yet known of their composition or constitution. The toxins vary in the intensity of their action, as do poisons of other origins, and for each species there is, for a given kind of animal, a certain minimum quantity which is capable of causing death under given conditions, a certain *minimum lethal dose*. With certain poisons, notably the toxalbumins (p. 572), the administration of repeated, gradually increased doses establishes a tolerance of the poison in the individual, so that in some instances ten times the lethal dose may be injected without causing a fatal result. The same is true, even more markedly, with toxins. An animal in which such a tolerance has been established is said to be **immunized** against the action of a given toxin or other poison. The immunity is also *specific*, i. e., it is established only for that particular toxin which has been administered.

As a certain definite, though small, amount of a toxin or other poison is necessary to produce lethal, or even toxic, effects in any animal, there exists a certain degree of **natural immunity** even in non-immunized individuals, to which the **acquired immunity** is super-added in those which have been immunized. This acquired tolerance in the case of exogenous poisons is usually small in comparison to the natural, but with the toxins and toxalbumins it is frequently very much greater. If the serum of an animal immunized by administration of a toxin be injected into another individual of the same species, immunity is also established in the second animal. The first is said to have been **actively** immunized, the second **passively**.

Although the *rationale* of the slow establishment of tolerance of arsenic or of the still greater tolerance of morphin has not been satisfactorily explained, there is no reason to believe that these are produced by any action occurring in the blood, but rather by some modification of these cell constituents upon which these poisons exert their action. It is also probable that in a certain degree the cells may become similarly protected from the action of certain toxins, particularly the intracellular toxins which are more slowly liberated on destruction of the bacterial cells. But the fact that a solution of a toxin, when mixed *in vitro* with the serum of an immunized animal and injected in sufficient quantity into a non-immunized animal, fails to produce the toxic effects which it does produce when injected without such admixture proves that some substance has been formed in the serum which enters into combination with the toxin to produce an inert combination.

Any agent which deters the action of the bacteria or of their toxins in the system is called an **anti agent**, or **anti body**. The **antitoxins** are anti bodies acting as above indicated upon the toxins, both being in all probability chemical individuals. The antitoxins are therefore only efficient in conditions of **toxæmia**, acting upon soluble toxins as in diphtheria.

Cytotoxins — Lysins — Agglutinins — Precipitins.—In producing immunity the antitoxins are consumed, and the action between antitoxin and toxin takes place in certain quantitative relations. Therefore the neutralization of toxin by antitoxin may be considered as a purely chemical process, comparable to the neutralization between acids and bases. But there are other substances produced in blood serum which effect immunity by destruction of bacterial and other cells, or by establishing conditions unfavorable to their development. The power of the leucocytes to absorb and, as it were, digest bacteria and other foreign cells in the blood, referred to as **phagocytosis**, was the earliest observed action of this character, which, however, differs in its nature from the more distinctly chemical process of cell destruction caused by certain more recently discovered soluble agents.

While human blood may, with suitable precautions, be transfused from the circulation of one individual to that of another without the occurrence of any untoward symptom, the transfusion of blood from one species of animal into the circulation of another of a different species is followed by toxic effects, prominent among which are the formation of clots and the occurrence of hæmoglobinuria, which indicate that the blood of a given kind of animal contains some substance which exerts a disintegrating action upon the red corpuscles of the blood of animals of different species. That this **hæmolytic** action is only indirectly dependent upon morphological elements, and is caused by a substance in solution; is shown by the fact that it is exerted *in vitro* by the filtered serum, the liquid becoming reddened by solution of the hæmoglobin liberated by disintegration of the corpuscles, which also diminish in number. It has also been demonstrated by bacteriological methods that normal blood serum, and milk also, is to a certain extent destructive of bacterial cells.

Substances which cause such destruction of cells are called **cytolsins**, or **cytotoxins**. Those which act upon blood corpuscles are distinguished as **hæmolysins**, while those affecting bacteria are called **bacteriolysins**.

The cytolytic action of blood serum, whether hæmolytic or bacteriolytic, is greatly increased by immunization, the increase being in both cases specific. Thus, after repeated injections of small quantities of ox blood in man, the serum of the human blood becomes much more actively hæmolytic to the corpuscles of ox blood, but not to those of other kinds of animal, than is that of normal human blood. Similarly, after repeated, graduated injections of cultures of the typhoid bacilli, the serum of the blood of the animal so immunized exhibits a greatly increased bacteriolytic action to the typhoid bacilli, but to those bacteria only. From these facts, and from the further fact that more than one cytolytic activity may be developed in the same serum, it may be inferred that the several lysins are distinct substances, which are produced in greater abundance during immunization.

Cytolysis by immunized sera is not the result of the action of a single substance, but of the joint action of two substances. If an activated hæmolytic serum be heated to 60° it loses its activity, but it again becomes active when mixed with normal serum. There are therefore two participants in the action: one a substance destroyed by heat, and therefore said to be **thermolabile**, which exists in normal serum, and another, capable of withstanding a temperature of 60°, and therefore said to be **thermostable**, which is produced during immunization.

A similar participation of two agencies in bacteriolysis is demon-

strated by what is known as **Pfeiffer's phenomenon**: The serum of an animal immunized to cholera exhibits very little bacteriolytic action *in vitro* to the cholera *spirillum*, but becomes actively destructive thereof either when injected into the peritoneal cavity of the animal or when mixed *in vitro* with normal serum.

That participant in effecting cytolysis which exists in the normal serum, that which is thermolabile, is called the **complement**, or **addiment**, or **alexin**. That which is developed during immunization is known as the **immune body**, or, because it is theoretically supposed to act as a means of union between the complement and the cell (see below) the **intermediate body**, or the **amboceptor**.

As antitoxins, which oppose the action of toxins, may be developed by immunization, so **antihæmolysins** may be similarly produced, which oppose the action of hæmolysins.

Agglutinins do not destroy blood corpuscles or bacteria, but cause them to agglutinate, or "clump" together. Marked agglutination of blood corpuscles is produced by toxalbumins, and has been observed in a case of poisoning by potassium chlorate.

Bacterial agglutinins are developed by immunization, and are specific in their action. These facts are utilized in the **Widal test** for typhoid fever, in which the result is considered as affirmative of the existence of the disease when clumping and loss of motility of the bacteria are observed in a mixture of the serum of the patient and a boillon culture of typhoid bacilli.

Precipitins.—The serum contains substances which form clouds or precipitates with certain constituents of the sera of animals of different species. This action, very slight with normal blood, may be greatly increased by a method akin to immunization. Thus if a rabbit receive six or eight intravenous or intraperitoneal injections of human blood at intervals of two or three days, the serum obtained from the blood will produce a distinct precipitate when mixed with a clear and highly diluted solution of human blood in normal salt solution. This action is specific within certain limits. The serum of the "humanized" rabbit, while producing a decided precipitate with human blood, gives but a faint reaction with that of certain monkeys, a mere cloudiness with those of the horse, ox, sheep and dog, and no effect with those of the many other kinds of blood which have been examined. Whatever it is that reacts with the precipitin withstands desiccation and putrefaction, as the reaction is given by dried or putrid blood. These facts are utilized in the "precipitin test" for human blood.

Chemical Theory of Anti Bodies—Ehrlich's Theory.—This theory was first advanced by Ehrlich in explanation of the method of assimilation of food materials by cells. The cells are supposed to be made up of two parts: (1) a central portion, consisting of a great

number of molecules of complex structure and great variety, whose interaction upon each other and upon the foodstuffs constitute the reactions of cell metabolism; (2) a peripheral portion consisting of molecules having groups capable of entering into combination with affinitive groups of the foodstuff molecules, brought to them by the nutrient circulating fluids, and thereby "anchoring" these, and subsequently transferring them to the central molecules, to be by them elaborated.

These anchoring, or **haptophorus groups** ($\alpha\pi\tau\epsilon\iota\nu$ = to fasten), of the peripheral molecules are supposed to be of different kinds, having different affinities, for the anchoring of the several varieties of food molecules, fats, carbohydrates, etc., and are considered as analogous to the lateral chains of cyclic organic compounds, hence the theory is also known as the "**side chain theory.**" For example: In phthalamic acid (formula, p. 478), the carboxyl constituting one lateral chain and the amido group contained in the other are each capable of reacting with such other molecules as contain groups which are reactive with them, and of so fixing other groups to the central ring. A closer analogy is found in the more complex morphin molecule, whose characteristic action upon the cells of the respiratory center apparently depends upon a linking action with some constituent of the cells through the phenolic hydroxyl which is one of its lateral chains (formula, p. 567), for when this is closed, as in morphylsulfuric acid (p. 563), the so modified morphin molecule, otherwise unchanged, no longer exerts this action.

The lateral chains are called **receptors**, of which the haptophorous group may constitute only a part, more or less influenced in its affinities by the remainder of the chain, just as in the two lateral chains of phthalamic acid the amido group would constitute one haptophorous group, uninfluenced by the methylene which forms the remainder of the chain, while in the carboxyl, which is the second receptor, the hydrogen owes its anchoring power, or reactivity, to association with oxygen.

In order that the food molecule may be fixed to the haptophorous group of the cell molecule, it must itself possess a group affinitive with the anchoring group of the receptor, and this correlation between the haptophorous groups of cell and food molecules must extend to similarity of stereometric conformation, if this may vary, for, as we have seen (p. 600), the cells of certain bacteria can assimilate sugars and other optically active substances of one conformation, but not their stereoisomeres.

To explain the action of toxins and antitoxins by this theory, it is assumed that the toxin molecules also consist of two parts, one a **toxophorous group**, by which the toxin exerts its characteristic action,

the other a haptophorous group. It is further assumed that the latter resembles in its conformation the haptophorous group of some food molecule sufficiently to permit of union with some of the receptors of cell molecules of a susceptible animal, and that by this means the toxin molecule may become attached to the cell, and by its toxophorous group exert its destructive influence upon the central molecules of the cell. As certain animals are naturally immune to certain toxins, it is inferred that in them no such correlation between haptophorous groups of cell and toxin exists. If the toxin injected into a susceptible animal be virulent, it is so because a great number of toxin molecules become so attached to the cells upon which they act, and the animal dies. But with a less degree of virulence, although the death of the individual does not result, the nutrition of the affected cells is seriously impaired, not only by the specific action of the toxin, but also because the toxin molecules occupy a sufficient number of those receptors of the cell which are affinitive to a given kind of food molecule to cause what might be called starvation of the cell in regard to that nutrient material. The receptors occupied by toxins have become useless, and are thrown off by the cell, which, being capable of regeneration of its parts, seeks to supply the loss by the formation of new receptors of the same kind, and, as is well known, in all such processes of repair there is not only production but overproduction. The excess of receptors so produced are then thrown off by the cell, and, being contained in the plasma, constitute the antitoxins, the free receptors blocking the haptophorous groups of the toxin molecules, and thus preventing their attachment to the cells, as the blocking of the hydroxyl of morphin prevents its action.

The serum from an actively immunized animal confers temporary passive immunity upon an animal into whose circulation it is injected, because free receptors are thus supplied. Such immunity is not produced unless the immune serum is injected before the toxins have become attached to the cells, and its degree is dependent upon the number of free receptors thus supplied by the immune serum.

The theory also assumes that there are more than one type, or order, of side chains, capable of anchoring food molecules, those of the first order, referred to above, being the simplest. The receptors of the second order not only fix the food molecules, but also exert a certain degree of preparatory, or digestive, action upon them. They are assumed to have, besides a haptophorous group, a **zymophorous**, or **toxophore** group, which produces an enzyme-like material, which acts upon the food molecule after it has become fixed by the haptophorous group. Receptors of this order also fix foreign cells, bacterial or corpuscular, which they destroy, and when they do so are thrown off from the cell, when repair and hyperplasia occur, and the free

receptors then thrown off by the cell constitute the agglutinins and precipitins, and possibly also certain lysins.

Receptors of the third order are those which are chiefly efficient in cytotoxicity. They possess two haptophorous groups, one of which is competent to anchor food molecules or foreign cellular elements, the other to fix enzyme-like bodies normally existent in the blood. When bacteria or foreign corpuscles encounter these receptors they are fixed by the appropriate haptophores, while the second group takes up the enzyme-like body, which then becomes active. Here again there are exfoliation of the occupied receptors, hyperplasia, and discharge of the excess of new receptors. These, when free, constitute the immune bodies, or amboceptors, while the enzyme-like bodies are the complements or addiments, the two together acting upon foreign cells to destroy them, before they become attached to the haptophores of the cells. The union of cell, amboceptor and complement is analogous to the union of two organic molecules through a connecting group which frequently takes place in organic syntheses, as in the numerous condensations which are produced by formic aldehyde by means of the CH_2 group (p. 301).

PHYSICO-CHEMICAL EXAMINATION OF BLOOD.

The more accurate methods of blood analysis, including those for the examination of the blood-gases, which are used in scientific investigation, are quite intricate, and demand close observance of details and considerable manipulative skill. As their description would require much space, and as they are not used for clinical purposes, the student is referred to more comprehensive treatises for an account of them. While the methods of microscopical examination of the blood for clinical purposes have been greatly perfected, and have led to valuable results, there is very little worthy of consideration in the way of chemical methods for this use. We have accurate methods for determining the physical qualities of specific gravity, freezing point, and electrical conductivity, methods of determining the reaction, which leave much to be desired, and methods of determining the quantity of hæmoglobin, some of which are accurate but difficult, others more easily conducted, but affected with large factors of possible error.

Specific Gravity.—(1) *Hammerschlag's method*, which depends upon the fact that a drop of an immiscible liquid will remain suspended in a liquid whose sp. gr. is equal to its own. A mixture is made of chloroform, sp. gr. = 1.526 and benzene, sp. gr. = 0.889, in such proportions that the sp. gr. of the mixture is about 1.050 to 1.055, and a drop of the blood is allowed to fall into it. If the

blood-drop sink more benzene is added, if it float, more chloroform, until the blood-drop remains suspended. The sp. gr. of the mixture is then determined, and is equal to the sp. gr. of the blood.

(2) *By direct weighing.*—Capillary tubes are used, drawn out at the ends, which are about 12 cm. long, and have internal diameters of 1.5 mm. in the middle, and 0.75 mm. at the ends. These are weighed empty, and also filled with water; the difference being the weight of water which the tube contains. The water is then blown out, and the tube filled with blood and again weighed. Subtraction of the weight of the empty tube from this last weight gives the weight of the blood. The sp. gr. is calculated, as usual, by dividing the weight of the blood by that of the water.

Freezing Point and Electrical Conductivity.—The freezing point of the defibrinated blood is determined by the method described at p. 68. The student is referred to works upon electro-chemistry for descriptions of the apparatus and methods used to determine electrical conductivity.

Reaction.—Determinations of the degree of alkalinity of the blood must be made as soon as possible after the sample is removed from the circulation to avoid as much as possible the minus error due to diminution of alkalinity (p. 667). *Lowy's method* is probably the least open to objection. A flask is used having a long neck, upon which are two marks, one at 45 cc., the other at 50 cc. This is filled to the 45 cc. mark with a one-fourth per cent. solution of ammonium oxalate, and 5 cc. of blood are drawn directly from the blood-vessel into it to the 50 cc. mark, and the contents mixed. The liquid is then titrated with a N/25 solution of tartaric acid (3 gm. tartaric acid to the litre), using a lacmoid paper saturated with strong magnesium sulfate solution as an indicator. One cc. of this solution is equivalent to 0.0016 gm. of NaHO; therefore the number of cc. used, multiplied by 200, gives the alkalinity in parts p/m of NaHO.

Hæmoglobin.—Of the chemical methods of determination of the quantity of hæmoglobin the best consists in incinerating the dried blood and determining the quantity of iron, from which the proportion of hæmoglobin is calculated.

Of the optical methods the most accurate is probably the spectrophotometric method of Vierordt, or one of its modifications, which depends upon measurement of the proportion of light of a certain wave-length absorbed in passing through a layer of a definite thickness of the blood, diluted in known proportion. This method, besides yielding accurate results, has the advantage that by it the proportions of oxyhæmoglobin, reduced hæmoglobin and carbon monoxid hæmoglobin may be determined in the same sample. It

requires, however, a spectroscope specially adapted to the purpose. (See Neubauer and Vogel, *Harnanalyse*, 10th ed. pp. 680-696.)

Colorimetric methods depend upon comparison of depth of color of the specimen of unknown content with standards of known content or value. When such comparisons are made between layers of equal thickness of solutions equal in transparency of the same substance, very slight differences in shade may be easily distinguished, and accurate results may be obtained. These conditions are fulfilled in the *hæmatinometer* of Hoppe-Seyler and its modifications, in which the depth of color of the blood, diluted in known proportion, is imitated in the comparison apparatus, with a solution of pure, crystallized hæmoglobin of known strength. When the two samples have precisely the same shade, the proportion of hæmoglobin in the comparison sample of known content will equal that in the diluted blood. To avoid the inconvenience of preparing the hæmoglobin solution, which does not keep, a solution of carbon monoxid hæmoglobin of known content, which is permanent, may be used, if the precaution be taken of converting the hæmoglobin in the blood sample into carbon monoxid hæmoglobin by passing CO through it before making the comparison.

The different forms of clinical colorimeters, known as *hæmoglobinometers*, such as Fleishl's, Dare's, Oliver's, Taylor's and Gower's, are all open to the objection that the comparison of tint is made with colored glasses, or with solutions of colored substances other than the blood-coloring matter, and consequently not identical in quality with it. While these instruments and to a less degree, the forms of clinical blood-testers depending upon determinations of opacity or of specific gravity, may afford comparative results of value to the clinician, they are not to be depended upon for accurate work. For the technique of clinical blood examination the student is referred to the excellent article by Dr. Camac in Wood's *Handb. of the Med. Sc.* 2d Ed. II. 37-71.

CHANGES IN COMPOSITION OF THE BLOOD IN DIFFERENT PARTS OF THE CIRCULATION.

As the blood-circulation is the channel through which the materials for the nutrition and functioning of the different parts of the body are carried to them, and by which the waste products of their activity are removed, a study of the variations in the composition of the circulating medium in its passage through different organs under varying conditions may well be expected to throw light upon the nature of normal and pathological chemical processes. Unfortunately, the difficulties in the way of experimentation are great, and

but little has yet been accomplished; the chief impediment being the difficulty of obtaining specimens of blood from the two sides of the organ under investigation, which are comparable with each other. The abstraction of any notable quantity of blood from the circulation at a given point, or the ligation of an efferent vessel and the consequent stasis in the organ at once produce pathological conditions. These difficulties have been in part overcome by "perfusion" experiments, in which the defibrinated blood of a recently exsanguinated animal is caused artificially to circulate through a given isolated organ, the liver for example, maintained at the body temperature. Analytical methods are then applied to samples of the unperfused and perfused blood, suitable for the determination of those constituents which are the subject of the enquiry.

The situations which have been the most frequently under investigation with regard to blood changes in them are the hepatic, the pulmonary and the renal circulations, and that in muscular tissue. Changes in the blood in the kidneys may be inferred from the composition of the urine, and will be considered under that head. The chemistry of the blood changes in the lungs is a portion of that of respiration (see pp. 686-692).

CHANGES IN THE LIVER.

We have seen that the secretion of the liver, the bile, plays but a secondary part in the processes of digestion, and is mainly excrementitious in character. On the other hand, as all the products of digestion which are absorbed from the alimentary canal by the blood are carried by the portal vein to the liver, mixed with the venous blood from the spleen and pancreas, and, after passage through the hepatic circulation, are discharged into the general circulation by the hepatic veins, and as, moreover, the liver is furnished with blood for its own nutrition by a separate supply through the hepatic artery, it would seem, *a priori*, that the liver should act as an adjunct to the digestive apparatus in being the seat of further chemical changes in the products of digestion, preparatory to their utilization in the tissues. That foreign substances absorbed from the intestine are modified chemically in their passage through the liver is shown by the fact that many poisons, not only metallic poisons, such as arsenic, copper and lead, but also alkaloidal poisons, such as morphin, strychnin, atropin, etc., when injected into the portal vein, act with only one-half to one-third the intensity as when injected in like amount into the jugular vein. The putrid products of intestinal origin are also modified in the liver. The normal portal blood of the dog has double the toxic power of the blood of the hepatic veins of the same animal when in-

jected into the peripheral circulation of rabbits. The liver has also been shown to be the situation in which some of the most important syntheses which occur in the economy take place.

In considering the blood changes which take place in the liver it is proper to consider briefly the

Chemistry of the Liver Cells.—The proteins which have been obtained from hepatic tissue, freed from blood and bile, are: an albumin, coagulating at 45° ; a globulin, coagulating at 75° ; a nuclealbumin, coagulating at 70° ; a protein related to the coagulated proteins, insoluble in dilute acids or alkalies at room temperature, but soluble as albuminate when heated with alkalies, and at least two, probably more, proteins containing iron. Of these last, one is apparently an albumin, others are certainly nucleoproteids, one of which, containing 1.45 per cent of phosphorus, is split by boiling water with formation of a nucleoproteid richer in nucleic acid, which is precipitable by acids, and yields a pentose, l-xylose, and xanthin bases on further decomposition. The occurrence of these iron-containing proteins in the liver cells, in which they exist in foetal life in larger proportion even than in adult life, is of interest in connection with the excess of iron left on decomposition of blood pigment in the liver, not accounted for in the bile and in the biliary pigment (p. 641), and with the formation of hæmoglobin. Iron, even in the form of salts of the metal, but better in that of organic combination, is absorbed, increasing in amount in the liver, even if administered hypodermically. But, as the iron of inorganic compounds is apparently not capable of elaboration directly into hæmoglobin, these ferruginous proteins are probably intermediate products, from which the blood pigment may be formed, either in the liver or elsewhere. Similar iron-containing proteins exist in the spleen.

The **carbohydrates** of the liver are glycogen and glucose. Glycogen is a substance closely related chemically to starch (p. 321), which exists in many situations in the body, notably in the liver, in muscular tissue, and in embryonic tissues, in each of which it is formed independently. The quantity of glycogen in liver tissue is influenced by several conditions. The average proportion is 12 to 40 p/m. With a diet rich in carbohydrates it may rise as high as 120 to 160 p/m. Under these conditions the glycogen content increases gradually, reaching its maximum in about 14 to 16 hours after the meal. With violent muscular activity it disappears entirely from the liver first, and subsequently from the muscles also, and that more rapidly in animals of small size than in larger ones. In rabbits under the influence of doses of strychnin sufficient to cause tetanic spasms, but insufficient to cause death, the liver glycogen disappears in 3 to 5 hours. The quantity of glycogen in the liver is also diminished, with

accompanying glycosuria, by the action of poisons other than strychnin, which do not cause tetanus, such as arsenic, antimony and phosphorus. The degree of protective action of the liver against poisons, above referred to, is directly proportionate to the quantity of glycogen present. In fevers the glycogen-content of the liver is diminished.

The proportion of glucose in liver tissue during life appears to be about 2 to 6 p/m. It rapidly increases in amount after death at the expense of the glycogen, and determinations of relative amounts of glycogen and glucose must be made immediately after death, the activity of the diastatic enzyme being arrested by plunging the organ into boiling water immediately on excision.

The **fats** in the liver exist in microscopic droplets, or in drops of larger size, deposited in the liver cells, in the proportion normally of 20 to 35 p/m of the organ. The amount is increased after meals to an amount dependent upon the fat-content of the diet. The amount is more greatly increased in fatty infiltration, to 190 to 240 p/m, when the proportion of water is correspondingly diminished, while the amount of other solids remains at about the normal. In fatty degeneration the proportion of fat is less than in fatty infiltration, although greater than normal, 80 to 90 p/m, while the proportion of water is increased, and that of solids other than fat is notably diminished. Lecithins are present in liver tissue in the proportion of about 23 p/m.

The **extractives** include xanthin bases, in the proportion of 4.5 p/m of dried tissue, urea, uric acid, cystin, leucin, tyrosin, inosite, and paralaetic acid.

The **blood changes** which occur in the liver, and the relations of that organ to metabolic processes, may be considered under five heads: (1) Formation of Bile, (2) Modifications of Proteins, (3) Modifications of Fats, (4) Action on Carbohydrates, and (5) Liver Syntheses.

That the bile is produced at the expense of the blood is a proposition which hardly requires demonstration, and it follows as a necessary corollary that in the liver the blood is modified by subtraction of those substances from which the bile constituents are there elaborated. The formation of the biliary salts is one of the synthetic processes of the liver. Their amido acid components, glycocholic and taurocholic, are products of general nitrogenous metabolism, the latter deriving from the cystin complex. Of the origin of cholic acid nothing is known with certainty, but from what little is known of the constitution of this acid it would appear that a carbohydrate origin is probable, and possibly there exists some relation between its formation and that of cholesterol (p. 642). The bile pigments, on the other hand, originate by an analytic process, the decomposition of the blood pigments (p. 640). Cholesterol is met with in all cells, either free or in combination, frequently in its esters, and is particularly abundant in the white

substance of brain tissue, of which it constitutes about one quarter of the total solids. Whether it is an essential constituent of the cells or a catabolic product is undetermined, but in any event it is apparently separated from the blood as the latter in the liver.

Little or nothing is known of the nature of the processes to which the fats are subjected in the liver, or of the products of such actions if any occur.

Of the actions of the liver upon the products of protein digestion there is likewise but little known, beyond the fact that dogs soon die with toxic symptoms, which have been ascribed to the action of ammonium carbamate, when fed upon meat after the establishment of Eck's fistula, by which the portal blood is discharged directly into the vena cava. The liver proteins are themselves quite readily decomposed by aseptic autolytic digestion, with formation of products similar to those produced by hydrolysis of proteins by acids. The proteins may also undergo a decomposition in the liver, the nature of which is unknown, except that the formation of glycogen is one of its results (below).

The action of the liver upon the carbohydrates has been the subject of more extended investigation, but, although the glycogenic function of that organ is well established, there still remains much that is uncertain regarding hepatic action in carbohydrate metabolism.

The products of digestion of carbohydrates brought to the liver by the portal blood consist of glucose, fructose, galactose and maltose. Saccharose and lactose when injected into the circulation are eliminated in their own form, but maltose is inverted in the blood to glucose. The three monosaccharids are therefore the raw materials with which the liver has to deal, and it is from them chiefly that glycogen is produced. The conversion of these hexoses into glycogen is a simple enough process from a chemical point of view: $n\text{C}_6\text{H}_{12}\text{O}_6 - n\text{H}_2\text{O} = n\text{C}_6\text{H}_{10}\text{O}_5$, but by what mechanism it is brought about in the liver cells is not known. It is certain also that not all of the sugar coming to the liver is converted into glycogen. A portion passes through the organ into the general circulation. The facts that fructose is converted into glycogen, and that this on hydrolysis yields only glucose show that the liver has the power of converting the $\text{CH}_2\text{OH.CO}$ —into the $\text{CHO}.\text{CHOH}$ —grouping, an action which is not peculiar to the liver cells, but is also produced by yeast and by chlorophyll. Nor is the power of glycogen formation peculiar to the liver, it is also exerted by muscular tissue and by embryonic tissues, and, indeed, appears to be possessed by all cells.

The question whether glycogen is produced in the liver from carbohydrate-free proteins has been the subject of much experimentation and discussion, and cannot be considered as determined, although the

weight of evidence appears to be in favor of the affirmative. It has been demonstrated that after a certain period of starvation glycogen disappears from the liver, and that if animals after such period of starvation be fed upon fibrin, the presence of glycogen in the liver can be demonstrated, and similar results are obtained after feeding with casein or gelatin, which contain no carbohydrate component. In diabetics upon a carbohydrate-free diet, glucose frequently exists in the urine in quantities which cannot be accounted for by the carbohydrate-content of either albumins or glycoproteids, but whether in these cases there is intermediate formation of hepatic glycogen has not been shown. No positive evidence of the formation of glycogen from fats in the liver is at hand, although it is said to occur in muscular tissue. It has also been shown that glycerol may be converted into glucose by the liver.

It has long been known that after death the proportion of glycogen in the liver diminishes and that of glucose increases, and that the change is arrested by plunging the organ into hot water. From these facts it may be inferred that glycogen is converted, post-mortem, into glucose by a hydrolysing enzyme in the liver. Whether or no a similar action occurs during life has been the subject of much controversy, the preponderance of the evidence being in favor of the affirmative of the question. When the liver is more or less completely excluded from the circulation, in geese, the glucose rapidly disappears from the blood, or, at least, is diminished to one-half or one-third. If the isolated rabbit's liver be perfused with Ringer's solution* notable quantities of glucose go into the solution, proportionate to the quantity of glycogen present in the liver, and being the greatest at first, diminishing subsequently. But if pure water be used in the perfusion, much glycogen goes into the liquid, but little glucose.

The part played by the liver, if any, in the different forms of glycosuria (p. 744) is still an open question, although it is certain that it is not the same in all the conditions in which that symptom exists. The blood normally contains 0.5 to 1 p/m of glucose, which is also present in traces in normal urine (p. 744), but when the proportion in the blood reaches 3 p/m the urine contains notable quantities of sugar; glycosuria exists. The power of the kidneys to prevent the passage into the urine of more than traces of sugar is therefore limited; and glycosuria may be caused either by a diminution of this power below the normal, or by an increase of sugar in the blood. The former condition is known to exist only in a form of artificial diabetes, produced by the administration of phloridzin,

* A solution which is considered as most suitable to preserve the life of the tissues, consisting of 100 cc. of 0.75 per cent NaCl soln.; 5 cc. of 0.25 per cent CaCl₂ soln.; 2.5 cc. of 0.5 per cent NaHCO₃ soln.; and 0.75 cc. of KCl soln.

which is a glucosid yielding a hexose other than glucose (p. 467) on its decomposition, and causing the formation in the system of glucose from protein material. Other glycosurias depend upon hyperglykæmia. This may, in turn, be due to one of three causes, either (1) the passage from the alimentary canal, through the liver, and into the general circulation of an abnormally large amount of sugar; (2) the formation in the liver, or elsewhere in the system, of an increased quantity of sugar; and, (3) an inability on the part of the system to utilize the amount of sugar normally produced. The first cause is certainly operative in *alimentary glycosuria*, due to a diet inordinately rich in assimilable carbohydrates. It is probable that, even under normal conditions, a portion of the sugars of the portal blood pass through the liver unchanged, and with an increased richness of the portal blood in carbohydrates a larger proportion will naturally escape the retaining action of the perfectly normal liver. Or this power may be pathologically diminished, as is probably the case in the milder forms of diabetes, in which the glycosuria readily disappears upon regulation of the diet, and also in some forms of chronic poisoning. The second cause is operative in glycosuria attending cerebral and nervous lesions, including the artificial diabetes caused by puncture of the floor of the fourth ventricle. It is not possible to exclude this cause also, as one of the factors in the severer forms of true diabetes, in which the daily elimination of sugar may go as high as 500 to 1,000 grams.

There is also diminution in the power of the system to consume the carbohydrates in true diabetes, as well as in the glycosuria attending diseases of the pancreas, and in the severe artificial diabetes following extirpation of that organ. Pancreatic diabetes is developed in animals only after complete extirpation of the pancreas. If a small portion of pancreatic tissue be, at the time of the operation, transplanted to the subcutaneous tissue, glycosuria does not occur, but it does after removal of this minute "artificial pancreas." The influence of the pancreas in sugar metabolism seems to be exerted to aid or provoke muscular glycolysis through the formation of an internal secretion, an activating agent of the same character as secretin (p. 626), and, like it, not an enzyme, as it is thermostable and soluble in alcohol. Extract of muscular tissue, when mixed alone with glucose solution, produces only a slight diminution of reducing effect of the sugar, but on addition of pancreas extract in suitable quantity, glycolysis becomes greatly activated, and the reducing power diminishes rapidly.

Liver Syntheses.—One synthetic process occurring in the liver, the formation of biliary acids from their components, has already been mentioned (pp. 640, 696), and the liver exerts its protective

action in the retention or neutralization of poisons, in some cases at least, by synthetic reactions.

Two poisons which are neutralized in certain amounts in the liver in this manner are phenol and morphin, by conversion into the inert monophenyl- (p. 470) and monomorphylsulfates (p. 563), or, more properly, the sodium or potassium salts of these acid esters. These are instances of a number of other reactions of the same, truly synthetic, type: $C_6H_5.OH + H_2SO_4 = C_6H_5.O.HSO_3 + H_2O$, by which toxic substances having phenolic hydroxyls, normally produced in the intestine by putrefactive processes, are converted into inert ester sulfates. Thus phenol, cresols, ortho- and paradiphenols, indole (indoxyl) and skatole (skatoxyl) are normally converted into the form of the conjugate compounds in which they are eliminated in the urine. The sulfates, or other oxidized sulfur compounds, required to unite with the phenolic substances, undoubtedly have their origin in the oxidation of the cystin complex of the proteins, but to what extent this oxidation takes place in the liver is uncertain. That it does occur there, and that the synthetic union takes place there has been shown by perfusion experiments, in which solutions of phenol and of cystin added to blood give rise to the formation of the ester sulfate in traversing the liver. A very similar synthesis also occurs, probably in the liver, between phenolic compounds and glucuronic acid (p. 348), which originates indirectly from glucose (p. 732), the conjugate glucuronates so formed being also eliminated by the urine.

Although it is doubtful whether uric acid is formed synthetically in the mammalia, there is abundant evidence that in birds, whose urine contains ammonium urate in large amount, the greater part of the uric acid is thus produced in the liver, from ammonium salts and from urea. In normal geese the elimination of uric acid is increased by administration of ammonium salts or of urea. In the same animals, after extirpation of the liver, the elimination of uric acid is greatly diminished, and that of ammonia is correspondingly increased, while at the same time the urine contains notable quantities of lactic acid. Uric acid has been produced by perfusing goose livers with blood containing ammonia and lactic acid. The elimination of uric acid by birds is increased by administration of ammonium lactate, of arginin, and of mixtures of urea with various aliphatic acids, notably oxy- and dibasic acids containing three carbon atoms, such as lactic, tartronic and malonic acids. In the formation of uric acid from the dibasic acids, it is probable that these are first converted into tartronic acid, which, uniting with urea forms tartronylurea, or dialuric acid (p. 527), which, in turn, combining with a second molecule of urea, forms uric acid, a synthesis, reminding one of that by which uric acid is artificially synthetized from malonylurea (p. 529). There is also

evidence that uric acid is formed from amido acids, glycocoll, leucin and aspartic acid in birds. It is uncertain whether or not in this method of formation deamidation of the amido acid, as glycocoll is deamidated to glycollic acid: $\text{CH}_2\text{NH}_2.\text{COOH} + \text{H}_2\text{O} = \text{CH}_2\text{OH}.\text{COOH} + \text{NH}_3$, is an intermediate step.

The formation of urea, which undoubtedly takes place in the liver, although it also occurs elsewhere in the system, is frequently referred to as a synthesis, although the reactions involved, being dehydrations so far as they are understood, are analytic, not synthetic, in character. The parent substances from which urea is thus produced are ammonium carbonate, ammonium carbamate, and the amido acids.

The conversion of ammonium carbonate into urea: $\text{OC}(\text{O}.\text{NH}_4)_2 = \text{H}_2\text{N}.\text{CO}.\text{NH}_2 + 2\text{H}_2\text{O}$, is a simple dehydration, easily effected *in vitro* (p. 403). That a similar reaction occurs in the liver, not only with the carbonate but also with other ammoniacal salts convertible into the carbonate by oxidation, has been demonstrated by perfusion experiments, and by the fact that in animals the portal blood always yields a larger amount of ammonia than does that of the hepatic veins. In the human subject the fact that in atrophy and in cirrhosis of the liver the elimination of urea is diminished and that of ammonia is increased, is an indication that in these conditions the normal conversion of ammoniacal compounds into urea by the liver is interrupted.

Ammonium carbamate has been found to be a constant constituent of the blood and of the urine, and it also yields urea by simple dehydration: $\text{OC} \begin{smallmatrix} \text{NH}_2 \\ \text{O}.\text{NH}_4 \end{smallmatrix} = \text{H}_2\text{N}.\text{CO}.\text{NH}_2 + \text{H}_2\text{O}$. It is also converted into urea, by dehydration, by the alternating galvanic current, a process which involves alternate oxidation and reduction. That the formation of urea from ammonium carbamate occurs in the liver has been demonstrated by observations upon Eck fistula dogs (p. 681), which, upon a protein diet, exhibit symptoms similar to those caused by intravenous injection of ammonium carbamate in normal animals, and in which administration of the same substance by the stomach causes like symptoms, which are, however, not produced in normal dogs under these conditions.

Carbamic acid is amido-formic acid (p. 411), the first term of series of mono-amido-fatty acids. Other amido-acids of the same series, such as glycocoll and leucin, and of the succinic series, as aspartic acid, are also undoubtedly intermediate products in the formation of urea. On oxidation in alkaline solution these substances yield carbamic acid, and, on the other hand, they are constant products of decomposition of albumins by the action of oxidizing agents, or of mineral acids, as well as by that of proteo-

lytic enzymes (p. 579), but to what extent they are thus formed in the system is undetermined. It cannot be doubted, however, that the amido-acids are decomposed, with formation of urea, probably with ammonium carbamate as an intermediate product, and that such formation takes place to a notable extent in the liver. It has been shown that glycocoll, leucin and aspartic acid, contained in arterial blood, which is made to traverse the isolated livers of dogs, are converted into urea or into some substance closely related to it. Another fact in support of the view that urea is produced from leucin in the liver is that, while this amido-acid is not found in normal urine, it makes its appearance there in notable quantity, while the proportion of urea is correspondingly diminished, in yellow atrophy and in acute phosphorus poisoning, in both of which conditions the function of that organ is seriously interfered with.

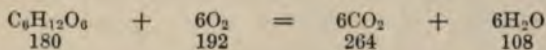
CHEMISTRY OF RESPIRATION.

The function of respiration is a physico-chemical one, the purpose of which is the introduction of oxygen into the system, and the removal of carbon dioxid and water therefrom. In so far as it is chemical, the subject may be considered under the following heads: (1) changes in composition of the air; (2) changes in composition of the blood-gases in the lungs; (3) tissue-respiration.

Changes in Air.—The average composition of dry atmospheric air, in volumes, corrected for 0° and 760 mm. barometric pressure, is: Oxygen—20.95, nitrogen—79.02, carbon dioxid—0.03, disregarding traces of other gases. The proportion of carbon dioxid varies from the above percentage in confined spaces (p. 355), and the air always contains varying quantities of vapor of water (p. 150). The expired air varies somewhat in the relative proportions of its constituents. Its average composition is, however: oxygen—16.03, nitrogen—79.59, carbon dioxid—4.38; and it is saturated with vapor of water at the temperature of the body, about 36°, and the barometric pressure. It will be seen that the proportion of nitrogen, which is a mere diluent, remains practically unchanged, and that the changes which the air undergoes in respiration consist of the subtraction of 4.92 volume-per cent. of oxygen, and the addition of 4.35 volume-per cent. of carbon dioxid and of a quantity of vapor of water, varying with the degree of saturation of the inspired air. With an increased degree of humidity of the inspired air the elimination of water by the skin and kidneys is increased.

That the oxygen taken into the system is utilized in processes of oxidation which take place in the tissues, and only to a limited extent in the lungs and blood, is now generally admitted. If the

oxygen taken in were entirely used for the oxidation of carbon, and if there were no source of oxygen other than the inspired air, the volume of oxygen removed from the inspired air should equal the volume of carbon dioxid added to it, as one molecule of oxygen produces one molecule of carbon dioxid. But the volumes are not equal, and neither of the above conditions exists. All tissues and organic food constituents contain hydrogen as well as carbon, and a portion of the oxygen is used to oxidize this to water. On the other hand, they all contain oxygen, as well as carbon and hydrogen, which supplements the oxygen derived from the air. Thus 180 grams of glucose produces by complete oxidation 264 grams of carbon dioxid, and 108 grams of water, for which 288 grams of oxygen are required, of which the glucose itself furnishes 96 grams, or one-third of the amount:



Moreover, carbon dioxid and water are not the only products of oxidation formed in the body: urea, for example, is a product of oxidation of the proteins. Thus the relation of oxygen consumed to carbon dioxid produced depends upon many conditions, and there is always an apparent loss of oxygen. This relation is known as the **respiratory quotient**, and is obtained by dividing the CO_2 produced by the O_2 consumed. Thus in the above proportions: $\frac{4.35}{4.9} = 0.88$. The fats contain 10.73 to 11.91% of oxygen, the proteins 21.5 to 23.5%, and the carbohydrates 51.17 to 53.33%, while the amount of oxygen required for the oxidation of their hydrogen is, for 100 parts each: of fats, 97.3 to 98.8; of proteins, 52.0 to 58.4, and of carbohydrates, 51.17 to 53.3. It is clear, therefore, that the carbohydrates contain sufficient oxygen for the oxidation of their hydrogen, while the proteins and fats require additional oxygen for that purpose, and that, consequently, the respiratory quotient will vary with the composition of the diet. It also varies with the amount of muscular activity, increase of which is attended with increase of oxidation of carbohydrates, proteins and fats, and with marked increase of production of carbon dioxid.

In considering the method of interchange between the gases of the blood and those of the air, it must be remembered that this exchange takes place between the blood and the air contained in the alveoli, and that this is not completely changed in respiration. Therefore, the composition of the alveolar air, which is the mixture formed by diffusion between the air remaining in the alveoli after expiration with that taken in during inspiration, is of importance in connection with the method of gas interchange. The composition

of alveolar air in the human subject can only be implied by calculation; but experiments upon animals have shown it to contain 3.6 to 3.8 volume-per cent. of carbon dioxid and about 16 volume-per cent. of oxygen, corrected for 0° and 760 mm.

Gases of the Blood.—The gases which the blood gives off when it is brought into a vacuum consist of oxygen, carbon dioxid, nitrogen, and traces of argon. The amount of nitrogen, including argon, is about the same in arterial and venous blood in different parts of the circulation, i. e., from 1 to 2 volumes in 100 volumes of blood. It probably takes no part in the chemical processes of the body. The blood-gases in which interest centers are, therefore, oxygen and carbon dioxid. The methods of absorption or elimination of these gases, and the form in which they exist in the blood may be either physical or chemical. That is to say, they may pass between blood and air by simple diffusion, or by a so-called "vitalistic" process, which, if it be not physical, must be chemical; and they may exist in the blood in simple physical solution, or in a form of chemical combination. To determine which of these methods are operative, and in what degree, is a subject requiring both physical and chemical investigation. We briefly recall here the laws governing the absorption of gases by liquids:

When a gas is in contact with a liquid it may either dissolve in or combine chemically with the liquid. In either case it is said to be **absorbed**. If in physical solution it is said to be **dissolved**, if in chemical combination it is said to be **combined**.

The **co-efficient of absorption** of a gas is the volume of that gas, reduced to 0° and 760 mm. Hg, absorbed by unity volume of the liquid under a pressure of 760 mm.; and it varies with the temperature. Thus the coefficient of absorption of carbon dioxid in water is 1.185 at 10° , which means that 1 cc. of water at that temperature, will absorb 1.185 cc. of carbon dioxid.

The *weight* of gas which a given *volume* of liquid will *dissolve* at a given temperature is directly proportionate to the pressure. But as the volume of a gas, at a given temperature, varies inversely as the pressure, the *volume* of gas dissolved is independent of the pressure; and the *density* of the dissolved gas is in constant relation to that of the undissolved gas in contact with it. Or, in other words, the *pressure* or *tension* of the dissolved gas is the same as that of the free gas in contact with it. If this equality be disturbed from any cause, as by variation of temperature, the gas passes into or out of solution, from the higher to the lower pressure.

The quantity of gas dissolved diminishes with increase of temperature, as the elastic force of the gas increases.

When several gases are dissolved in the same liquid, each is dis-

solved as if it were alone, its volume being estimated at the pressure which belongs to that gas in the mixture. This *partial pressure* is to the total pressure as the volume of the gas in question is to that of the mixture under the same conditions. The partial pressure may be calculated by the formula $PP = \frac{V \times P}{100}$, in which V is the volume-per cent. of the gas in question in the mixture, and P the total pressure in mm.

The pressure (tension) of a gas in solution may be experimentally determined by bringing the solution in contact with gaseous mixtures containing known and varying proportions of the gas in question. If the pressure in the solution be less than the partial pressure in the mixture, gas will be dissolved, while gas will be given off from the solution if the reverse be the case. By analyzing the gaseous mixtures, that one is found in which the gas under investigation has neither increased nor diminished, and the partial pressure of the gas in it equals the pressure of the gas in the solution.

Oxygen.—The proportion of oxygen in arterial blood is about 21.6 volume-per cent. That in venous blood differs in different parts of the venous system. An average of many analyses of the blood of the right heart gives its oxygen-content as 14.85 volume-per cent. As the coefficient of absorption of oxygen in water at 35°, the body temperature, is 0.0277, the maximum amount of that gas that could exist in solution in water is 2.77 volume-per cent., and it may be assumed that for simple solution the action of the blood plasma is the same as that of water. Indeed, analyses of the gases from blood-plasma and blood-serum have shown the presence of 0.26 volume-per cent. of oxygen.

It follows that almost all of the oxygen in the blood exists in some form of chemical combination in the blood-corpuscles; and we have seen that hæmoglobin is capable of forming such a combination. It has also been shown that a solution of freshly prepared, pure, crystallized oxyhæmoglobin behaves in the same manner as fresh, defibrinated blood under the influence of reduced pressures. The dissociation of oxyhæmoglobin, whether in solution or in defibrinated blood, under reduced pressures also shows, by the manner in which it takes place, that the oxygen is present in a "loose" form of chemical combination. The disengagement of oxygen does not begin immediately with reduction of pressure, indeed, this may be reduced to about half an atmosphere without any notable disengagement of oxygen. Operating at 35° to 39°, the pressure may be lowered to 410 mm. Hg without any reduction of the oxygen-content of the arterial blood, at 375 to 365 mm., it is slightly reduced, at 300 mm., the reduction is notable, and in the vacuum of the mercury pump the oxygen is completely given off.

As to the process by which the oxygen passes from the alveoli into the blood: if the oxygen pressure in the blood be less than the oxygen partial pressure in the alveoli the physical action of diffusion is sufficient to transfer the gas in the direction of the lower pressure, but if the reverse be the case some other force must be in operation. We have seen that the volume-per cent. of oxygen in alveolar air is 16, which, at 760 mm., represents a partial pressure of 121.6 mm. The oxygen pressure in arterial blood has not been determined with equal certainty. By some observers this value is given as 75 to 80 mm., but others have obtained results as high as 110 to 144 mm. The weight of evidence appears to be in favor of the lower figures, and of the consequent view that the passage of oxygen from the alveoli to the blood is a purely physical process.

Carbon Dioxid.—The proportion of carbon dioxid in arterial blood is 30 to 40 volume-per cent., usually nearer 40. The proportion in venous blood is about 48 volume-per cent., and in asphyxia it may rise as high as 69.21 volume-per cent. If the plasma and corpuscles be separately examined, both are found to give off carbon dioxid, and that in the relative proportion of one-third of the entire amount from the corpuscles and two-thirds from the plasma. If blood be introduced into a vacuum it bubbles and gives off all of its gas, but if blood serum or plasma be subjected to the vacuum a portion of their carbon dioxid is retained, and is only liberated upon addition of an acid. Therefore, a part of the carbon dioxid of the blood exists in the corpuscles in "loose" combination, while in the plasma a part exists in that condition, or in solution, and a part in "firm" combination; and the blood corpuscles act like the acids, in that they liberate this latter portion from its combination. Indeed oxyhæmoglobin is capable of expelling carbon dioxid from alkaline carbonates in a vacuum. Carbon dioxid apparently exists in the corpuscles in two forms of combination. It is in part combined with hæmoglobin (p. 659), probably with its protein component. Another portion enters into reaction with the alkaline phosphates, which are present in sufficient quantity to form alkaline bicarbonates and monophosphates.

The proportion of carbon dioxid existing in the plasma in "firm" combination has not been accurately determined. Undoubtedly it represents the alkaline carbonates resulting from decomposition of the bicarbonates (see below), but the quantity of these cannot be determined either from the quantity of carbonate left on incineration, or from the degree of alkalinity of the plasma, because the former result in part from the combustion of other organic compounds of the alkali metals, and the latter is due in part to the presence of other alkaline compounds. Nor can the amount of carbon dioxid

which is not removed by the vacuum, and only after addition of an acid, be considered as representing the whole of the firmly combined carbon dioxid, because other substances exist in the plasma, such as the globulins, which decompose a part of the alkaline carbonates in a vacuum. It can only be stated that of the 20 to 32 volume-per cent. of carbon dioxid in the plasma, from 5 to 9 volume-per cent. is retained in a vacuum, and probably represents a large part of the alkaline carbonates existing in the blood as bicarbonates. Such being the case, a notable proportion, at least, of the loosely combined carbon dioxid must exist in the plasma in the form of bicarbonates ($2\text{NaHCO}_3 = \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}$), from which it is liberated in vacuo by the action of weakly acid substances, such as the globulins. Indeed, the greater part of the carbon dioxid in the plasma is probably present in the form of bicarbonates, a view which is further supported by the notable diminution in the amount of carbon dioxid in the plasma in acidism (diminished alkalinity of the blood), caused either by administration of mineral acids, or by increased acid formation in diabetic coma, in which the total carbon dioxid in the plasma may fall as low as 2 to 3 volume-per cent., the excess of acid taking up the bases.

A portion of the carbon dioxid of the plasma is also in simple solution. By the method described on page 689 the carbon dioxid pressure in arterial blood has been found to be 2.8% of an atmosphere, equivalent to a pressure of 21 mm., of Hg, while in the blood of the right heart $3.81\% = 28.95$ mm. Hg, and $5.4\% = 41.04$ mm. Hg have been found. Comparative results between the carbon dioxid pressures in the blood and in the alveolar air are, however, not concordant. According to some observers, the blood carbon dioxid pressure is the higher, and the exit of carbon dioxid is consequently a purely physical process; while, according to others, the alveolar partial pressure is the higher, and a "vitalistic" action of the epithelial cells is invoked to overcome the higher pressure. The oxygen entering the blood is also supposed to play a part in expelling carbon dioxid from its chemical combinations.

Tissue Respiration, or internal respiration, takes place between the blood in the capillaries and the tissues, through the lymph, and consists in the passage of oxygen from the blood to the tissues, in which the oxidations of the body occur, and the passage of the carbon dioxid and water resulting from such oxidations in the opposite direction. As oxygen enters into combination in the tissues, and is thereby removed from solution, and as carbon dioxid is there produced, it is clear that the oxygen pressure in the tissues must become less than that in the blood, while the carbon dioxid pressure in the tissues must tend to increase, and therefore the simple physical

process of passage from the greater to the lesser pressure must be in operation.

LYMPH—CHYLE—TRANSUDATES—EXUDATES.

The **lymph** is a circulating medium intermediate between the blood and the cells. The endothelial cells of the heart and blood-vessels and those of the splenic pulp are the only ones in the body which come into immediate contact with the blood; all other cells derive the materials for their nutrition, including oxygen, from, and discharge their catabolic products into the lymph, between which and the blood a corresponding interchange takes place. The lymph circulation differs from that of the blood principally in that the flow is only in one direction, from the smaller to the larger vessels. The lymph is formed by filtration and osmotic pressure from the blood plasma in the capillaries into the lymph spaces, the smallest, blind ramifications of the lymphatic system, and, having performed its function in the interchange of material with the cells, finds its way back to the venous system, after having passed through gland-like enlargements, called the lymphatic glands, or lymphatic nodes, principally by way of the thoracic duct and the right common lymphatic trunk. Only a portion of the catabolic products collected by the lymph is carried to the venous system by the larger lymphatic trunks, the greater part passing directly from the smaller lymphatics into the capillaries and venules.

Distinction is made between four varieties of lymph: (1) *Tissue lymph*, that contained in the intercellular spaces throughout the body; (2) *Circulating lymph*, that passing slowly through the lymphatic vessels towards the veins; (3) *Chyle*, the circulating lymph collected from the intestinal mucous membrane during digestion, particularly of fats; (4) *Serous lymph*, the liquids normally contained in the pleural, peritoneal and pericardial cavities, in the cerebral ventricles, and the cerebro-spinal fluid.

The physical properties and composition of the tissue, circulating and serous lymphs are essentially identical. The lymph contains corpuscles, a few red blood-corpuscles and many leucocytes, which latter are formed in the lymphatic glands, in the spleen and in the thymus. The fluid portion of the lymph, the lymph plasma, is, like the blood plasma from which it is derived, clear, faintly yellow, alkaline from the presence of Na_2CO_3 and Na_2HPO_4 , salty in taste from the presence of about 0.6 p/m of NaCl , of specific gravity slightly lower than that of blood plasma, because of less content of solids, and coagulable from the presence of fibrinogen and fibrin ferment. Serous lymph, however, although containing fibrinogen, contains no fibrin ferment, and therefore does not coagulate spontaneously. Serous lymph also contains less protein than tissue or circulating lymph. The constituents of

lymph plasma are the same in kind as those as the blood plasma. Quantitatively the proportion of solids, 35.7–57.2 p/m, and notably of proteins, 37.5 p/m, are less than those in blood plasma.

The **chyle** is the lymph produced in the lacteals of the intestinal mucosa during digestion of fats. Practically all of the fat is absorbed by this channel. The chyle is milky in appearance from the presence of oil globules in suspension, and it differs from the clear lymph which is carried by the same vessels when fat absorption is not taking place, solely in the presence of notable quantities of fat. The maximum amount of fat found in the chyle obtained from a fistula in the human subject during fat absorption was 47 p/m, the fluid from the same fistula during fasting containing 0.6 to 2.6 p/m of fat.

Transudates and Exudates.—Speaking strictly, the lymph is a transudate, being formed by filtration and osmosis from the blood, but the application of the term has come to be limited to pathologically increased deposits of more or less modified serous lymph in the lymph spaces or cavities, produced by increased blood pressure, by pathological modification of the walls of the vessels, or by alterations in the blood, but not by inflammatory processes. The typical transudate is that of œdema, whether of ascites, anasarca, hydrothorax, hydrocele, etc. The fluid of œdema is colorless or pale-yellowish, or, with attendant icterus, yellow or brown, alkaline, containing very few leucocytes or red cells, and sometimes flakes of fibrin, of low sp. gr., not exceeding 1010, and containing a low proportion of proteins, 1.5 to 20 p/m.

Sometimes a transudate may be milky in appearance, and may contain from 4 to 43 p/m of fat, suspended in fine oil globules, from admixture of chyle. The transudate of hydrocele differs from the typical transudate in being more highly colored, in having a higher sp. gr., 1016 to 1026, in containing a larger proportion of solids, to 60 p/m, and of proteins, to 50 p/m, and frequently in containing a large amount of cholesterolin, suspended in glistening, tabular crystals. The fluid of ovarian cysts contains metalbumin and paralbumin (p. 594).

Exudates differ from transudates in being the products of inflammatory processes, in being cloudy or opaque from the presence of a much greater number of leucocytes and other morphological elements, in being yellow, dirty-greenish, or reddish in color, in being of higher sp. gr., 1016 to 1030, in containing a larger proportion of solids, to 90 p/m, and of proteins, to 60 p/m, and in being spontaneously coagulable.

Pus is an exudate modified by proteolytic bacterial action. It is creamy and mucoid in consistency, usually alkaline, although sometimes acid and having the odor of butyric acid, usually of sp. gr.

about 1030, but varying from 1020 to 1040. It consists of two parts, whose relative proportions vary within wide limits. A liquid portion, the *liquor puris*, or pus serum, somewhat resembling the blood serum in appearance and in composition. It contains no fibrinogen, and does not coagulate spontaneously. It contains a nucleoalbumin or nucleoproteid, which is precipitated by acetic acid, and is very difficultly soluble in excess of the acid.

The pus cells are modified leucocytes, containing a large proportion of protein, particularly of nucleoproteids and nucleins. Among the former the most abundant is the "hyaline substance of Rovida," which swells to a slimy mass with a 10 per cent solution of NaCl. They contain no nucleohiston, or histon, and no thrombin or prothrombin. They contain a proteolytic enzyme and the products of its action, albumoses, peptone, and xanthin bases, and, in the pus of abscesses of long standing, leucin and tyrosin. They also contain notable amounts of cholesterol, lecithins, cerebrin, as well as fats, soaps, and free fatty acids.

URINE.

The urine is the only pure excretion of the body, its formation has but one object, the removal of waste material, and it is the principal channel of exit from the body of water, of solid products of disassimilation, and of foreign substances, medicines, poisons, etc., more or less altered by chemical change in the body. As the urine is obtainable without difficulty, and as it varies in composition with variations in the chemical processes of the body, analysis of the urine affords the readiest means of obtaining insight into the nature of normal chemical processes in the body, and of pathological departures therefrom. The form in which medicinal substances are eliminated in the urine is also of interest to the pharmacologist, as indicating the changes which they have undergone in their passage through the system, and their probable method of action. The toxicologist finds in the urine the last traces of poison undergoing elimination.

PHYSICAL CHARACTERS.

Consistency.—The normal urine of man and of the carnivora is clear and transparent when voided. On standing it usually soon becomes cloudy, and a light flocculent cloud of "mucus," the "nubecula" of older authors, which contains epithelium, mucus corpuscles, and urates, separates and remains suspended in the liquid. The urine of the herbivora is cloudy when voided and is alkaline in reaction, and human urine when alkaline in reaction is also cloudy. When the

urine is not perfectly transparent its cloudiness may be due to the presence of morphological elements and casts in suspension, or to the presence of phosphates or urates which have become insoluble. Phosphates thus separate from the urine when the reaction becomes subacid, and they disappear on addition of an acid. Urates are deposited from hyperacid urines and do not dissolve on addition of acid to the urine. Generally the urine has no viscosity, but alkaline urines containing pus are sometimes thick and "stringy." When shaken with air, the bubbles soon disappear from the surface of normal urine, but in urines containing sugar or bile the froth persists for quite a time. In the rare condition of chyluria, depending upon the presence of filaria in the blood, the urine is turbid and has the appearance of milk.

Quantity.—The average normal quantity of urine passed by an adult in 24 hours is 1,200 to 1,500 cc., being somewhat less in the female than in the male; and in children absolutely less, but relatively to weight more than in adults. The quantity is increased with increase of the amount of liquids ingested, and diminished when the secretion of perspiration is increased. **Polyuria**, i. e., increased quantity of urine, occurs pathologically in diabetes mellitus, in which it is frequently 3,000 to 5,000 cc., sometimes 10,000 to 25,000 cc., and even more, in diabetes insipidus, during absorption of large effusions, in granular atrophy of the kidneys, and in nervous diseases, such as hysteria, chorea, and epilepsy. **Oliguria**, i. e., diminished quantity of urine, occurs in continued fevers, in acute nephritis, in chronic parenchymatous nephritis, in cardiac diseases, towards the fatal termination of all diseases, in surgical shock, and under all conditions in which water is otherwise disposed of, as in diarrhœa, after hæmorrhages, and during formation of dropsical effusions.

Specific Gravity.—The specific gravity of the mixed urine of 24 hours, when the amount is normal, is 1,015 to 1,025. The "corrected" specific gravity is the observed sp. gr., corrected to what it would be if the quantity were the normal amount of 1,200 cc., and is obtained by the formula $D = \frac{Q \times d}{1200}$, in which Q is the quantity of urine in 24 hours, and d the last two figures of the observed sp. gr. Example: Q = 600 cc., d = 20, then $600 \times 20 \div 1200 = 10$; sp. gr. = 1,010. The sp. gr. gives a rough indication of the quantity of total solids. The last two figures of the sp. gr., multiplied by 2.33 gives, in normal urine, approximately the amount of total solids p/m. Example: sp. gr. = 1,017, $17 \times 2.33 = 39.61$ grams of solids in 1,000 cc. This rule does not hold good if the urine contains sugar or albumin. Generally the sp. gr. varies inversely as the quantity. But in diabetes mellitus the quantity

is large and the sp. gr. high. The quantity is diminished and the sp. gr. is low in obstructive suppression, in the later stages of fatal diseases attended with defective elimination of solids, in œdema, and in diseases attended with copious diarrhœa, vomiting or sweating. For methods of determining sp. gr., see page 11.

Color.—The color of the normal urine varies from a very pale yellow to a brownish-orange, being darker when concentrated than when dilute, and also darker when strongly acid. Clinically, urines may be divided, according to color, into pale, normal, high-colored, and dark. The urine is pale when its quantity is increased. Normally-colored urines are of negative significance only. High-colored urines owe their color to the presence of the normal urinary coloring-matters in increased amount (p. 725). They occur in all forms of acute febrile disease, and indicate increased activity of tissue change. Concentrated urines are high-colored. Dark urines vary in color from orange-red to black. Exceptionally the urine may be dark from the presence of greatly increased quantity of normal coloring-matter, as in beri-beri; but usually a dark urine owes its color to the presence of an abnormal pigment: red or reddish-brown from the presence of blood-pigment; brownish-yellow, greenish-brown or dark-brown from bile coloring-matters; smoky, violet or black from derivatives of carboic acid, resorcinol, salol, or salicylic acid; golden-yellow from santonin; yellow, changing to blood-red with alkalis, from chrysophanic acid (rhubarb, cascara, senna). In chyluria the urine is white and milky.

Odor.—When freshly voided, the odor of the urine is faint and aromatic, but on standing it rapidly develops the urinous odor, and finally that of ammonia. Certain food and medicinal substances, such as asparagus, copaiba and turpentine, communicate peculiar odors to the urine. In diabetes the urine has a faint, but distinct, "sweet" odor.

Reaction.—The reaction of the urine depends largely upon the nature of the diet. In herbivora it is neutral or alkaline; in the carnivora strongly acid. The urines of suckling herbivorous animals and that of adults during starvation, conditions in which the animals are practically carnivorous, are acid. The reaction of the normal human mixed urine of 24 hours is always acid. Samples collected at different times of the day may be normally acid, alkaline or amphoteric. After meals the acidity of human urine diminishes, and, during the period of greatest activity of stomach digestion, it may even become alkaline (p. 610). If the urine, after having been voided, is kept at the ordinary temperature, its acidity rapidly diminishes, and it becomes alkaline and ammoniacal from decomposition of the urea. It then becomes cloudy, from deposition of phosphates,

sometimes of calcium oxalate, and later of ammonium urate. The acidity of the urine may be increased by administration of dilute mineral acids, but not beyond a certain degree. It may be diminished by administration of dilute alkalies or of vegetable acids or their salts, which are oxidized in the system to carbonates. The acid reaction of the urine is due, to some extent, to the presence of carbonic acid, but principally to that of monometallic phosphates. Uric acid does not occur free, but in combination, in normal urine; therefore it does not contribute directly to the acidity, but indirectly it is largely concerned in the production of the acid reaction. The alkaline phosphates of the blood are converted into acid phosphates and urates by reaction with uric acid: $\text{Na}_2\text{HPO}_4 + \text{C}_5\text{H}_4\text{N}_4\text{O}_3 = \text{NaH}_2\text{PO}_4 + \text{NaC}_5\text{H}_3\text{N}_4\text{O}_3$; and a further formation of acid phosphate from alkaline phosphate results from the action of sulfuric acid, produced by oxidation of the sulfur of the proteins, and of hydrochloric acid reabsorbed with the peptones.

The acidity is more intense than normal in concentrated urines, in fevers, gout, acute articular rheumatism, leukæmia, scurvy, and sometimes in diabetes. The acidity of diabetic urine frequently increases after it is voided, with separation of crystals of uric acid, from the formation of acids by fermentation. The reaction may become alkaline from the presence of fixed alkalies, carbonates, or alkaline phosphates, or of volatile alkali, ammonium carbonate. Physiological subacidity or alkalinity is always due to the former, which are also the cause of the alkalinity occurring in anæmia, after cold baths, after absorption of alkaline transudates, and after administration of organic acids or mineral alkalies. Alkalinity from volatile alkali always results from decomposition of urea, which takes place in the bladder in cystitis.

The reaction of the urine has an important bearing upon the formation of calculi. Much the larger proportion of urinary calculi are either phosphatic or uric acid, and the conditions of reaction under which the two kinds are formed are the diametrical opposites; the deposition of uric acid requires a strongly acid urine, while the phosphates are deposited from subacid or alkaline urines. Uric acid calculi and "gravel" are more usually of renal origin, phosphatic calculi never. When, as frequently occurs, a uric acid calculus forms the nucleus of a large phosphatic calculus, the uric acid nucleus was formed in the kidney in a strongly acid urine, and, coming down into the bladder, has been the cause of a cystitis by mechanical irritation, which, in turn, has produced an alkaline or subacid urine, from which the phosphates have been deposited upon the uric acid nucleus.

The quality of the reaction is best determined in the usual way,

with litmus paper. If the reaction be alkaline the blued red litmus is allowed to dry in a place protected from acid fumes. If the color returns to red on drying the alkalinity is due to volatile alkali, while if the blue color persists, it is due to fixed alkali.

The determination of the degree of acidity cannot be accomplished in the usual way, by titration with standard alkaline solutions. As stated above, the acidity of the urine is due almost entirely to the presence of acid phosphates, notably of acid sodium phosphate, or monosodic phosphate, NaH_2PO_4 . But the urine also contains disodic (and dipotassic) phosphate, Na_2HPO_4 , whose reaction is faintly alkaline, the two salts being in varying proportion to each other. If now an alkaline solution, such as a N/10 solution of caustic soda be added to the mixture of the two salts in solution, the monosodic salt is converted into the disodic: $\text{NaH}_2\text{PO}_4 + \text{NaHO} = \text{Na}_2\text{HPO}_4 + \text{H}_2\text{O}$, and a time is reached when the proportion of the two is such that the reaction is not neutral, i. e., without influence upon the indicator, but amphoteric, i. e., turning red litmus blue and blue litmus red. As the measure of the degree of acidity of the urine is the amount of phosphoric acid (P_2O_5) present in monometallic phosphates, the determination of the acidity depends upon that of phosphoric acid in its two forms of combination, as monometallic and dimetallic salts. This is done by the Freund-Lieblein method: The total phosphoric acid (T) is first determined by the method described on p. 706. To another sample of 75 cc. of urine, 15 cc. of barium chlorid solution (122 gm. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ to the litre) are added, by which the dimetallic phosphates (M) are precipitated, while the monometallic phosphates (D) remain in solution. The mixture is shaken, and filtered and refiltered until the filtrate is clear. Sixty cc. of the clear filtrate, representing 50 cc. of urine, are taken for a second phosphoric acid determination by the same method. As in the treatment with barium chlorid, there occurs a partial conversion of one phosphate into another, by reason of which about 3% of the phosphoric acid of the dimetallic phosphate remains in solution as monometallic salt, a correction is here necessary, and is made by subtracting 3% from the result of the second determination. The corrected result (D) represents the phosphoric acid present in monometallic phosphates.

Freezing Point—Cryoscopy.—We have seen (p. 68) that the depression of the freezing point of a solution below that of the pure solvent is a measure of the osmotic pressure of the dissolved substances, and (pp. 67, 73) that the osmotic pressure at constant temperature is proportionate to the number of particles, molecules and ions, present in unit volume of the solution. Therefore the determination of the depression of the freezing point of urine below that of water, called a "cryoscopic examination," affords an excellent indication

of its concentration in both ionized and non-ionized constituents. While the depression of the freezing point of blood is almost constant at $\Delta -0.56^\circ$, that of the urine, which is more concentrated, is greater, and varies usually between $\Delta -1.3^\circ$ and -2.0° . When the urine becomes diluted, as after the ingestion of large amounts of liquid, Δ may fall to -0.1° , and when it becomes highly concentrated Δ may rise to -3.0° .

Electrical Conductivity.—The electrical conductivity of a liquid (p. 42) is proportionate to the number of free ions present (p. 74). It will therefore vary with variations in the proportion of electrolytes, such as mineral salts, which are present in the solution, but will not be affected by variations in the proportion of non-electrolytes, such as urea and the other organic constituents of the urine, except that these, by offering resistance to the passage of the current, produce a slight diminution of the total conductivity below that which would be observed with solutions of equal quantities of the same salts in the same volume of pure water. But, with this slight error, the determination of the conductivity of the urine gives an indication of its degree of concentration in mineral salts, and by comparison of the results obtained by this method with those of the cryoscopic examination it is possible to determine what fraction of the osmotic pressure is due to non-electrolytes and what to electrolytes. The chlorids in the urine constitute the greater part of the electrolytes present, and they are subject to wide variations, not dependent upon metabolic processes, but upon varying amounts of NaCl taken with the food. The sulfates and phosphates, on the other hand, are largely the products of metabolism of sulfur- or phosphorus-containing organic substances. Attempts have been made to study the variations in organic sulfur and phosphorus metabolism by determinations of electrical conductivity, subtracting from the results obtained the calculated conductivity due to chlorids, based upon chlorin determinations, but the results cannot be considered as having been satisfactory. It is to be expected, however, that the cryoscopic and conductivity methods will prove of considerable value in the future, as the mineral salts appear to have a greater influence upon the chemism of the body than they were formerly supposed to exert.

It is clear that the conductivity of the urine must vary at different times of the day, according to the quantity of electrolytes in the diet and the activity of their elimination. It is usually within the limits of $\kappa=0.0149$ and 0.0303 (pp. 42, 46, 74).

CHEMICAL COMPOSITION.

The constituents of the urine may be divided into two classes: normal and abnormal. Clinically some normal constituents, such as

sugar, which are present in healthy urine in quantities so small as to escape detection by the tests customarily used, but are greatly increased in disease, are ranked as abnormal constituents. It is clear that, as the normal constituents are constantly present, we can only obtain indications of clinical value by their variations in quantity. The mere presence in detectable quantity of the abnormal constituents indicates a pathological condition, the gravity of which is frequently proportionate to the quantity of the abnormal constituents voided. Quantitative determinations of both normal and abnormal constituents therefore constitute a large part of urine-analysis. As it has been found that the elimination of all constituents of the urine is subject to variation at different times of the day under different conditions of eating, sleeping, exercise, etc., quantitative results obtained with the morning urine are not comparable with those obtained from afternoon urine, indeed the only quantities which are comparable with each other are the amounts excreted in 24 hours, and *no quantitative determination should be made except with samples of the mixed and measured urine of 24 hours.*

The normal constituents of the urine are classified into the two groups of **mineral and organic.**

MINERAL CONSTITUENTS.

The mineral salts are chlorids, sulfates, and phosphates of potassium, sodium, ammonium, calcium, and magnesium, with traces of silicic acid. Of the bases sodium and potassium are the most abundant, and of the acidulous factors chlorin. In the urine of 24 hours the quantity of acid present is in excess of that required to completely neutralize the amount of base present, and that, notwithstanding the fact that a portion of the bases exist in organic combinations not here considered; from which it follows that a portion of the salts must be incompletely saturated, or acid salts, such as acid sodium phosphate, NaH_2PO_4 , and it is to these that the urine owes its acidity. It is convenient to classify the salts of the urine according to their acids, rather than according to their bases, into chlorids, sulfates and phosphates.

Chlorids.—The chlorids present are those of all the bases mentioned above, but sodium chlorid largely predominates, and it is usual to calculate all of the chlorin found on analysis as sodium chlorid. The usual amount of chlorids eliminated is from 10 to 15 gms. NaCl in 24 hours. It is, however, subject to great variations, chiefly due to differences in the quantity of salt taken with the food by different individuals. The elimination is less during the night than during the daytime. When NaCl is excluded from the diet its elimination by

the urine ceases before it disappears from the blood. Numerous determinations of chlorids in various diseased conditions have been made, but it must be remembered that the observed departures from the normal may be due in large part, if not entirely, to variations in the amount of salt ingested, or to removal of chlorids by other channels. The extremes of reported variations are from 0 to 50 gms. in 24 hours. Diminished elimination has been observed in acute febrile diseases, scarlatina, roseola, variola, typhus, typhoid pneumonia, yellow atrophy, in all acute renal diseases with albuminuria, in carcinoma of the stomach, gastric ulcer, anæmic conditions, rickets, melancholia, idiocy, dementia, chorea, paralysis, impetigo, pemphigus, during formation of exudates, with diarrhœa, and in chronic lead poisoning. Increased elimination occurs in acute diseases during reabsorption attended with diuresis, in diabetes insipidus, during the polyuria following attacks of epilepsy, and in general paresis when large amounts of food are taken.

The usual **methods of quantitative determination of chlorids** are by titration with silver nitrate solution, either by Mohr's or Volhard's method. The former is the most generally applicable if interfering substances be first removed. If the urine contain albumin, this is first removed by coagulation and filtration. Ten cc. of the albumin-free urine are placed in a platinum crucible along with about 1 gm. of pure (Cl-free) Na_2CO_3 and about 2 gm. pure KNO_3 , and evaporated to dryness. The residue is cautiously heated to fusion, cooled, dissolved in water, and faintly acidulated with HNO_3 . If bromids or iodids be present they must be removed at this point by adding dilute H_2SO_4 and a little sodium nitrite to the solution, and shaking it with successive portions of carbon disulfid until colorless. The aqueous solution is placed in a porcelain dish, with a similar dish containing an equal quantity of water alongside for comparison of tint; a few drops of neutral potassium chromate solution are added to the contents of each dish; and the silver solution is gradually added to the chlorid solution until, after stirring, it has a faint reddish tinge as compared with the contents of the second dish. The silver solution used may be either a N/10 solution, containing 17.00 gm. of pure, crystallized AgNO_3 to the litre, each cc. of which represents 0.00585 gm. NaCl in the 10 cc. of urine used; or a solution containing 29.054 gm. AgNO_3 to the litre, each cc. of which represents 0.01 gm. NaCl. The result, multiplied by 1/10 the quantity of urine in 24 hours, gives the daily elimination.

Volhard's method consists in precipitating the chlorids completely by an excess of silver nitrate (20 cc. of the second silver solution mentioned above) filtering, and determining the excess of silver salt in a portion of the filtrate by titration back with a solution of potas-

sium thiocyanate containing 8.3 gm. KCNS to the litre (2 cc. of which = 1 cc. AgNO_3 solution) using a solution of ammonio-ferric alum as an indicator, and subtracting this from the total AgNO_3 added.

Sulfates.—The sulfates of the urine are of greater physiological interest than the chlorids. The latter are not formed in the body, and variations in their elimination depend, practically entirely, upon variations in the amounts taken with the food and drink. The sulfates, on the other hand, are only present in the food and in natural waters in small amount, and the greater part of these salts in the urine are produced in the body by metabolism of the cystin complex of the proteins, and therefore variations in their elimination afford indications of the degree of activity of metabolic change of the organic compounds from which they are derived. The relation of nitrogen to sulfuric acid in the urine is quite constant at 5N to 1SO_3 .

A portion of the sulfuric acid thus formed by oxidation combines with the bases to produce sodium and potassium sulfates, with lesser amounts of calcium and magnesium sulfates, and, exceptionally, ammonium sulfate. These constitute the "mineral sulfates." Another portion combines, probably in the liver (p. 684), with phenolic compounds to produce the sodium and potassium salts of the "ester sulfates," or "conjugate sulfates" (pp. 541, 646, 728). Not all of the sulfur of the proteins is thus oxidized to sulfates, whether mineral or ethereal, but a portion is eliminated in organic combination, in a variety of substances, in which form it constitutes the "neutral sulfur" (p. 730). The average daily elimination of mineral sulfates, with a mixed diet, is 1.5 to 3.0 gms. SO_3 , that of ester sulfates 0.15 to 0.3 gm. SO_3 . The relation between these two forms is, however, quite variable, and the proportion of ester sulfates present indicates the degree of activity of putrefactive changes in the intestine, or of retention and absorption of their products, in the absence of administration of phenolic compounds, or the absorption of putrid products from other sources. The proportion of ester sulfates is increased in faecal retention, in obstructive jaundice, in septæmia, and in hypochlorhydria. In poisoning by phenols the mineral sulfates are reduced to zero, and the ethereal sulfates correspondingly increased. In diarrhoea both forms are diminished, while in acute leukæmia both are increased.

Analytically, sulfur is determined in the urine in three forms of combination, either directly or by difference: (1) As mineral sulfates, (2) as ester sulfates, (3) as neutral sulfur, and best by Folin's method.

Mineral sulfates.—To 25 cc. of urine, in a 250 cc. Erlenmeyer flask add 100 cc. of water and 10 cc. of dilute HCl (1 vol. conc. HCl to 4 vols. H_2O). If the urine be dilute, use 50 cc. urine and 50 cc.

water. To the diluted, acidulated and cold liquid add 10 cc. of a 5 per cent solution of BaCl_2 , without agitation or disturbance, drop by drop, and slowly. At the end of an hour, or later, the mixture is shaken up and the precipitate collected on a long-fibered asbestos film, in a porcelain Gooch crucible, with moderate suction. The precipitate is then washed with 250 cc. of cold water, dried, and ignited in the covered crucible, supported upon the lid of a platinum crucible, for about ten minutes.

Total sulfates.—To decompose the ester sulfates, 25 cc. of urine and 20 cc. of dilute HCl (1:4 as above), or, if the urine be dilute, 50 cc. of urine and 4 cc. of concentrated HCl , are gently boiled in a 250 cc. Erlenmeyer flask, whose mouth is covered with a watch-glass, for half an hour. The flask is cooled for two or three minutes in running water, and the contents diluted with cold water to about 150 cc. To this cold solution 10 cc. of 5 per cent BaCl_2 are then added, with the precautions mentioned, and the process concluded as above. The total sulfates, minus the mineral sulfates, gives the ester sulfates.

Total sulfur.—The organic sulfur is oxidized to sulfates by sodium peroxid: 25 cc. of the urine, or 50 cc. if very dilute, are measured into a 250 cc. nickel crucible, and about 3 gms. of sodium peroxid are added. The mixture is evaporated to a syrup, and then carefully heated until it solidifies, the latter heating occupying about fifteen minutes. The crucible is then cooled; the residue moistened with 1-2 cc. of water; about 7 gms. of sodium peroxid are sprinkled upon it; and the mixture heated to complete fusion for about ten minutes. After cooling, the contents of the crucible are heated with about 100 cc. of water for about half an hour, to dissolve the alkali and decompose the sodium peroxid. The mixture is then rinsed into a 450 cc. Erlenmeyer flask with hot water, and the bulk of the liquid made up to about 250 cc. Concentrated HCl is then slowly added to the almost boiling liquid, until the nickelic oxid just dissolves, which requires about 18 cc. of acid for 8 gms. Na_2O_2 . After a few minutes' boiling, the liquid should be perfectly clear, unless too much water or too little peroxid have been used in the final fusion. If not clear the liquid must be cooled and filtered. To the clear, acid solution 5 cc. of dilute alcohol (1 part alcohol to 4 parts water) are added and the boiling continued for about five minutes, to remove traces of chlorin. Ten cc. of 10 per cent BaCl_2 solution are then added, with the same precautions as above, and the mixture is left standing in the cold for two days, after which the process is concluded as above. The amount of neutral sulfur, as SO_3 , is obtained by subtracting the value obtained for the total sulfates from that for the total sulfur.

Phosphates.—The phosphates present in the urine are those of sodium, potassium, calcium and magnesia. The Na and K phos-

phates, which include the monometallic and dimetallic salts, are known as **alkaline phosphates** (p. 698), those of Ca and Mg as **earthy phosphates**. About two-thirds of the total phosphoric acid is contained in the alkaline phosphates, of which the sodium salts are greatly in excess of the potassium, and one-third in the earthy phosphates. The average elimination of phosphoric acid (P_2O_5) is 2.5 to 3 gm. per diem, but it may vary within normal limits from 1 to 5 gm. a day. This variation depends largely upon the nature of the diet, the amount being larger with an animal than with a vegetable diet, except the latter contain cereals, which are rich in phosphates, in large amounts. A notable quantity of phosphates are contained in food articles, both in alkaline and in earthy combination, of which the former are readily absorbed, while the latter, being soluble only in acid liquids, are in large part passed with the fæces. A part of the urinary phosphates are also formed in the system as products of oxidation of the phosphorus existing in the albumins, nucleoproteids, nucleins, protagon and the lecithins. The proportion between the amounts of nitrogen and of phosphoric acid eliminated, sometimes called the "relative value" of phosphoric acid, is calculated by the formula $N:P_2O_5::100:x$. Normally the value of x is from 17 to 20; thus, taking the average elimination of nitrogen as 14 gm., and of phosphoric acid as 2.5, the value of x would be 17.85. While variations in this relation depend, in some measure, upon differences in the composition of food articles ingested, they also depend upon differences in the character of tissue changes which may be exaggerated. The value of x , obtained by the above formula, would differ notably according as the N and P_2O_5 are derived by oxidation of albumins, on the one hand, or of other phosphorus-containing substances on the other:

	N	P	P_2O_5	x
Albumins	{ 15.60 . . 0.42 . . 0.96 . .	N: P_2O_5 ::100: 6.40		
	{ 17.60 . . 0.85 . . 1.95 . .	N: P_2O_5 ::100: 11.07		
Nucleohiston	16.86 . . 3.03 . . 6.93 . .	N: P_2O_5 ::100: 41.10		
Protagon	2.80 . . 1.23 . . 2.82 . .	N: P_2O_5 ::100:100.71		
Bone	6.44 26.76 . .	N: P_2O_5 ::100:415.52		
Lecithins	1.73 . . 3.84 . . 8.79 . .	N: P_2O_5 ::100:508.09		

It is evident from the above that an increase in the relative value of phosphoric acid may be expected under conditions involving either an increased tissue change in bone, with elimination of its phosphates, or increased metabolism of tissues rich in nucleated cells. Such is the case in starvation, in which both the absolute and relative elimination of phosphoric acid, as well as that of calcium compounds, are notably increased. With increased mental activity, also,

the elimination of earthy phosphates is increased, and that of alkaline phosphates diminished.

Pathologically the elimination of phosphoric acid is diminished in acute febrile diseases, chronic nephritis, amyloid degeneration of the kidney, hysteria, Addison's disease, acute yellow atrophy of the liver, and in lead poisoning. It is increased in convalescence from acute diseases, meningitis, epilepsy and leukæmia, and, particularly, in "phosphatic diabetes," in which the elimination of phosphoric acid may reach 8 to 9 gm. in 24 hours, and in which the other symptoms of diabetes are present, but there is no glycosuria. In diabetes mellitus the quantity of phosphoric acid is subnormal, particularly when the quantity of sugar is large.

The earthy phosphates only are concerned in the formation of calculi. So long as the reaction of the urine (p. 697) remains acid they are held in solution, but when the reaction becomes alkaline, or even on loss of CO_2 on exposure to air, the insoluble trimetallic salts are formed and deposited. Alkaline urines are, for this reason, almost always turbid, and become clear upon addition of an acid. It is in such urine that **phosphatic calculi** are always formed, usually about a nucleus of uric acid, or of a foreign body. If the alkalinity be due to the formation of ammonia, the **ammonio-magnesium phosphate**, or **triple phosphate**, $\text{Mg}(\text{NH}_4)\text{PO}_4$, is produced, either in the form of large, tubular crystals, or as a **fusible calculus**.

A process for the **quantitative determination of phosphoric acid** in the urine is based upon the formation of the insoluble uranium phosphate, and upon the production of a brown color when a solution of a uranium salt is brought in contact with a solution of potassium ferrocyanid. Four solutions are required: (1) *a standard solution of disodic phosphate*, made by dissolving 10.085 grams of crystallized, non-effloresced HNa_2PO_4 in H_2O , and diluting to a litre; (2) *an acid solution of sodium acetate*, made by dissolving 100 grams sodium acetate in H_2O , adding 100 cc. glacial acetic acid, and diluting with H_2O to a litre; (3) *a strong solution of potassium ferrocyanid*; (4) *a standard solution of uranium acetate*, made by dissolving 20.3 grams of yellow uranic oxid in glacial acetic acid, and diluting with H_2O to nearly a litre. Solution 1 serves to determine the true strength of this solution, as follows: 50 cc. of Solution 1 are placed in a beaker, 5 cc. of Solution 2 are added, the mixture heated on a water-bath, and the uranium solution gradually added, from a burette, until a drop from the beaker produces a brown color when brought in contact with a drop of the ferrocyanid solution. At this point the reading of the burette, which indicates the number of cc. of the uranium solution, corresponding to $0.1 - \text{P}_2\text{O}_5$, is taken. A quantity of H_2O , determined by calculation from the result thus obtained, is then added to

the remaining uranium solution, such as to render each cc. equivalent to 0.005 gram P_2O_5 .

To determine the **total phosphates** in a urine: 50 cc. are placed in a beaker, 5 cc. sodium acetate solution are added; the mixture is heated on the water-bath, and the uranium solution delivered from a burette, until a drop, removed from the beaker and brought in contact with a drop of ferrocyanid solution, produces a brown tinge. The burette reading, multiplied by 0.005, gives the amount of P_2O_5 in 50 cc. urine; and this, multiplied by $\frac{1}{24}$ the amount of urine passed in 24 hours, gives the daily elimination.

To determine the *earthy phosphates*, a sample of 100 cc. urine is rendered alkaline with NH_4HO , and set aside for 12 hours. The precipitate is then collected upon a filter, washed with ammoniacal water, brought into a beaker, dissolved in a small quantity of acetic acid; the solution diluted to 50 cc. with H_2O , treated with 5 cc. sodium acetate solution, and the amount of P_2O_5 determined as above.

Metallic Elements.—The metallic elements of urinary salts are sodium, potassium, calcium, and magnesium. Sodium and potassium are present, not only in combination with mineral acids, but also in organic combination, as in the urates. The daily elimination is equal to 2–3 gm. K_2O , and 4–6 gm. Na_2O ; or $K:Na::2.5:5$. Calcium and magnesium are present principally in their phosphates, in less amount as chlorids, and occasionally their urates are met with in calculi. About 1 gm. of Ca and Mg is eliminated in 24 hours, in the proportion of $\frac{2}{3}$ Mg and $\frac{1}{3}$ Ca.

NORMAL ORGANIC CONSTITUENTS OF THE URINE.

For purposes of investigation the normal organic constituents of the urine may be conveniently divided into three classes:

- (1) Organic compounds containing nitrogen;
- (2) Organic compounds containing sulfur; and
- (3) Organic compounds containing neither nitrogen nor sulfur.

Nitrogenous constituents are quite numerous, constitute almost the whole of the urinary solids, and differ from each other widely in the amounts in which they are eliminated. In this class are included: urea, ammonium salts, ammonium carbamate, creatinin, uric acid, xanthin bases, hippuric acids, oxaluric acid, allantoin, indoxyl and skatoxyl glucuronates, urochrom, etc., cystin, indoxyl and skatoxyl sulfates, taurocarbamic acid, chondroitin-sulfuric acid, oxy-proteic acid and alloxypoteic acid, of which the last six also contain sulfur.

Total Nitrogen—Nitrogenous Equilibrium—Nitrogen Distribu-

tion.—The normal elimination of nitrogen with a mixed diet is from 12 to 16 gms. in 24 hours. With a protein-rich diet it may rise to 18.2, while with a diet of fats and carbohydrates it falls from about 11 gms. to as low as 2.8 gms. per 24 hours.

Normally the elimination of nitrogen by the urine is increased by not too long continued ingestion of water in large quantity; during and after strenuous muscular exercise; with a diet excessively nitrogenous; and after ingestion of ammoniacal compounds; and it is diminished by deficiency of nitrogen in the diet; after free perspiration; and in some cases of normal pregnancy (see Urea, p. 711).

Pathologically it is increased in the early stages of all acute febrile diseases, except when these are attended by the formation of dropsical deposits or by diarrhœa; during reabsorption of dropsical fluids; in both forms of diabetes; and in chronic interstitial nephritis (see Urea, p. 711).

For the determination of total nitrogen 5 cc. of urine are placed in a long-necked Kjeldahl digesting flask along with 0.5 gm. of CuSO_4 and 15 cc. of concentrated H_2SO_4 . The flask is supported at 45° to the horizontal and gradually heated until white fumes are given off; 10 gm. of K_2SO_4 are then added, and the contents of the flask heated just short of boiling until almost colorless. After cooling, the contents of the digesting flask are transferred and washed into a distilling flask; the acid is nearly neutralized by the slow addition of NaHO solution (sp. gr. 1.24); a few pieces of granulated zinc are added, and then a moderate excess of NaHO solution, whereupon the flask is immediately connected with a bulb tube and condenser, so arranged as to deliver the distillate into a recipient containing 30 cc. of $\text{N}/5$ H_2SO_4 and a little lacmoid as an indicator. The distillation is continued until about $2/3$ of the liquid have passed over, when the excess of H_2SO_4 remaining in the recipient is determined by titration with $\text{N}/5$ NaHO solution. Each cc. of $\text{N}/5$ acid neutralized by the ammonia formed in the process corresponds to 0.0028 gm. of nitrogen in the 5 cc. of urine used. A blank process must be conducted with reagents alone to guard against error from nitrogen compounds in the reagents or in the air.

An animal organism is said to be in a condition of **nitrogenous equilibrium** when the quantity of nitrogen taken in with the food equals the quantity eliminated in the urine and fæces in the same period. The absolute quantity of nitrogen for this condition will vary with different individuals, and with the same individual at different times, the influencing factors being chiefly the health of the subject, the mode of life, and the composition of the dietary. In an individual receiving a diet of constant composition and containing sufficient nitrogen for the purposes of nutrition the nitrogen output will become

constant in from two to four days. By now varying the nitrogen intake, if necessary, to equal the output, and maintaining other conditions as nearly at equality as possible, the condition of equilibrium will be ultimately reached, it being remembered, however, that there is a tendency of the organism to adapt the nitrogen output to the intake, and that periods of 24 hours are not long enough for comparison during variation of the intake, as the output of one day is influenced not only by the intake of that day, but also by that of the preceding day. A healthy adult man can maintain nitrogenous equilibrium under usual conditions upon a diet containing 0.6 gm. of albumin or (as proteins contain an average of 16 per cent of N, or 1 N=6.25 protein) 0.096 gm. of nitrogen per kilo of body weight per diem. This is the lower limit of nitrogenous equilibrium in man, for when the intake is less than this equilibrium is no longer maintained, and the output becomes greater than the intake, the organism dissimilating its proper tissues to supply the deficiency of supply.

The study of the **distribution of urine nitrogen**, or the **nitrogen partition** of the urine, i. e., the relative proportions of the total nitrogen which are contained in the individual nitrogenous constituents, has only become possible recently for a few of those constituents which are the most abundant, by the invention of quantitative processes of sufficient accuracy. Those constituents which may now be so determined are urea, ammonia, uric acid and creatinin; the remainder of the nitrogenous constituents must still be classified under the head of "undetermined nitrogen." In studying the distribution it is also essential that the absolute amounts of the several substances be taken into consideration as well as their relative proportions, for it is clear that, with variations in the relative proportions of several substances, the absolute amount of any given one may be a constant or a variant, and moreover, a percentage which would be normal for a given value of total nitrogen would not be normal for another. Much work is now being done in this direction, and results of great interest are to be anticipated from investigations of variations in nitrogen partition, not only of normal, but also of abnormal urinary constituents. At the present time it may be said that Folin has established the basis of comparison for future investigations by fixing the normal nitrogen distribution, and the influence upon it of the composition of the dietary.

In a series of investigations with six normal persons, weighing about 70 kg. each, receiving a "standard diet," containing a liberal rather than a scanty allowance of protein, i. e., 119 gms. protein=19 gms. nitrogen per diem, over periods of five days, the following distribution of nitrogen was found:

	Total nitrogen	Urea nitrogen	Ammonia nitrogen	Creatinin nitrogen	Uric acid nitrogen	Undeter- mined nitrogen
Average	16.0	13.9	0.70	0.58	0.12	0.60
Minimum	14.8	12.8	0.55	0.50	0.08	0.41
Maximum	18.2	16.2	0.85	0.66	0.15	0.85

or in percentages of total nitrogen:

	Urea	Ammonia	Ammonia +urea	Creatinin	Uric acid	Undeter- mined
Average	87.5	4.3	91.85	3.6	0.8	3.75
Minimum	86.2	3.3	90.70	3.2	0.6	2.70
Maximum	89.4	5.0	92.60	4.5	1.0	5.30

Another series of determinations with four persons were divided into three periods of feeding. During the first of these the subjects received the same food as in the above experiments; during the second the diet was changed to a "starch-cream diet," containing only 1 gm. of nitrogen per diem; and during the third period the diet of the first was returned to:

	Total nitrogen	Urea nitrogen	Ammonia nitrogen	Creatinin nitrogen	Uric acid nitrogen	Undeter- mined nitrogen
Last day	16.1	14.1	0.50	0.55	0.22	0.70
First day	10.6	8.9	0.50	0.51	0.17	0.46
Second day	7.8	6.1	0.46	0.52	0.16	0.48
Third day	6.5	4.8	0.44	0.50	0.12	0.64
Fourth day	4.7	3.15	0.47	0.49	0.09	0.42
Fifth day	5.1	3.5	0.51	0.56	0.11	0.40
Sixth day	4.9	3.4	0.50	0.54	0.11	0.37
Seventh day	3.9	2.3	0.44	0.54	0.11	0.49
Eighth day	4.1	2.65	0.43	0.54	0.11	0.32
Ninth day	4.2	2.7	0.49	0.60	0.11	0.43
Tenth day	3.8	2.3	0.52	0.58	0.12	0.25
First day	9.8	7.3	0.76	0.60	0.18	0.91

or in percentages of total nitrogen:

	Urea	Ammonia	Ammonia +urea	Creatinin	Uric acid	Undeter- mined
Last day	87.5	3.2	90.7	3.4	1.4	4.5
First day	84.4	4.7	89.1	5.0	1.6	4.3
Second day	79.0	5.9	84.9	6.7	2.1	6.3
Third day	73.5	6.8	80.5	7.7	1.9	9.9
Fourth day	67.5	10.1	77.6	10.5	2.0	9.9
Fifth day	69.0	10.0	79.0	11.0	2.1	7.9
Sixth day	69.0	10.2	79.2	11.1	2.2	7.5
Seventh day	60.0	11.4	71.4	14.0	2.8	12.8
Eighth day	65.3	10.7	76.0	13.3	2.7	8.0
Ninth day	61.8	11.5	73.3	14.0	2.6	10.1
Tenth day	61.2	13.6	74.8	15.4	3.1	6.7
First day	74.9	7.8	82.7	6.1	1.9	9.3

The results in the four cases were quite concordant, and we have given the results of the last day of the first period, the entire second period, and the first day of the last period in one case only.

Comparison of the above figures shows that with nitrogen deprivation urea is diminished both relatively and absolutely; ammonia remains nearly constant absolutely, but is notably increased relatively; creatinin is slightly increased absolutely and greatly increased relatively; uric acid is diminished absolutely, but increased in about the same ratio relatively; while undetermined nitrogen is diminished absolutely, but increased relatively, with notable oscillations.

Folin, in interpreting these results and those of his other determinations, reaches the following conclusions:

"The distribution of the nitrogen in urine among urea and the other nitrogenous constituents depends on the absolute amount of total nitrogen present.

"The absolute quantity of creatinin eliminated in the urine on a meat-free diet is a constant quantity different for different individuals, but wholly independent of quantitative changes in the total amount of nitrogen eliminated.

"When the total amount of protein-metabolism is greatly reduced, the absolute quantity of uric acid is diminished, but not nearly in proportion to the diminution in the total nitrogen, and the per cent of the uric acid nitrogen in terms of the total nitrogen is therefore much increased.

"With pronounced diminution in the protein metabolism (as shown by the total nitrogen in the urine), there is usually, but not always, and therefore not necessarily, a decrease in the absolute quantity of ammonia eliminated. A pronounced reduction of the total nitrogen is, however, always accompanied by a relative increase in the ammonia-nitrogen, provided that the food is not such as to yield an alkaline ash.

"The absolute quantity of undetermined nitrogen decreases under the influence of the starch and cream diet, but in per cent of total nitrogen there is always an increase.

"Urea is the only nitrogenous substance which suffers a relative as well as an absolute diminution with a diminution of the total protein metabolism."

Ammonia.—It is believed that the ammonia which is eliminated in the urine represents that fraction of the product of protein decomposition which has escaped conversion into urea, presumably in the liver (p. 685). One cause which would operate to prevent such conversion would be the combination of ammonia in the form of ammonium sulfate or phosphate, which are not convertible into carbonate, as are the ammonium salts of organic acids. With a deficient nitrogen intake

the elimination of ammonia is unchanged in absolute amount, or is sometimes diminished, while its relative amount is increased. With excessive consumption of fats, which also occurs in persons with a large amount of adipose during starvation, more or less complete, there is marked increase in the elimination of urine ammonia. The ammonia-content of the urine is also increased by interference with the aëration of the blood, and it is supposed that in such cases the ammonia combines with the excess of carbon dioxide in the blood (see also Acetone, p. 753).

The **quantitative determination** of ammonia in the urine is by no means the simple proposition it would appear to be, the difficulty lying in the tendency of other nitrogenous constituents to undergo decomposition with formation of ammonia. All determinations made with the older processes of Schlösing, and Nencki and Zaleski, have been affected with a plus error from this cause, and those obtained with the more recent method of Shaffer are sometimes similarly vitiated.

The method of Folin is free from this source of error, as neither CaH_2O_2 nor BaH_2O_2 is used: To 25 cc. of the urine, 8 to 10 gms. of NaCl , 1 gm. of dry Na_2CO_3 , and 5 to 10 cc. of petroleum or of toluol (the last to prevent frothing) are added. Through the mixture, contained in a suitable apparatus, communicating with two absorbing vessels charged with a measured volume of $\text{N}/10$ acid, a current of air is driven at room temperature for one and a half hours, at the rate of about 600 to 700 liters per hour, after which the excess of acid is titrated back with $\text{N}/10$ alkali, using alizarin red as an indicator.

Urea.—Under usual conditions the absolute elimination of urea by a healthy man of about 70 kilos is from 30 to 35 gms. in twenty-four hours, with a mixed diet, and this constitutes from 86 to 90 per cent of the total nitrogen. With a diet containing an excessive amount of protein these figures may become still greater. With a diet poor in nitrogen, both the absolute and relative amounts are diminished notably, the former falling during six days from 19 to 3.5 gms. in 24 hours, and the latter from 84.5, progressively diminishing to 60 per cent of the total nitrogen. Under usual conditions urea is therefore the most abundant constituent of the urine, and the form in which most of its nitrogen is excreted, but it is possible that under conditions which are not normal, although they cannot be said to be pathological, this might cease to be the case, as it sometimes does under pathological conditions. As, with a continuance of low-nitrogen diet, or on diminution of nitrogen intake, the absolute and relative amounts of urea progressively diminish, while the relative amounts of ammonia and creatinin both increase, it is conceivable that, if the system can tolerate a further reduction of protein metabolism below that reached in the experiments reported, as in all probability it may, the relative

proportion of urea may fall below those of ammonia and of creatinin. In two instances at least this has been known to occur, so far as ammonia is concerned, in pathological urines: In one case 14.7 per cent of the total nitrogen was present as urea, and 40 per cent as ammonia. In the second case 4.4 per cent of the total nitrogen was in urea, and 26.7 per cent in ammonia.

The elimination of urea, like that of all constituents of the urine, normal or abnormal, is not the same in amount during all equal fractions of the twenty-four hours. The minimum elimination is in the early morning hours, and the maximum in the middle of the afternoon, if the principal meal be taken at noon.

The formation of urea from ammonium carbonate and carbamate in the liver has been referred to (p. 685). Although this is the only origin of urea which has been demonstrated, it is certain that it is neither the only seat nor the only method of production of urea, and it is probable that this substance is formed not only from the "circulating proteins," i. e., those contained in the blood and lymph, as its direct dependence upon protein intake shows it to be, but also from the "tissue proteins," i. e., those entering into the composition of the cells. Possibly it may be produced in part as a side product in the formation of creatinin, or of some of the several other substances from which the "undetermined nitrogen" is derived.

The view formerly entertained that uric acid constitutes an important intermediate stage in the formation of urea in the system has been greatly modified. It is now conceded that much the greater proportions of uric acid and of the xanthin bases are produced, in mammalian metabolism, from the nucleoproteids, as products of processes distinct and separate from that, or those, by which urea is produced.

On the other hand, it has been demonstrated, by experiments with perfusion of solutions of urates through kidneys and livers, and with the aseptic action of finely hashed "breis" of these and other organs upon the same salts, that urea may be produced from uric acid by these organs. It was found that the livers taken from digesting animals have the power of decomposing uric acid, with formation of urea, but that those of fasting animals have not. It was also found that the action of the same organ taken from different kinds of animals, and different organs from the same animal, differ in their action in this regard. As a rule, the kidney is the most active in its destruction of uric acid, and the liver next in activity. The livers of dogs and pigs decompose uric acid, while those of calves produce it. The two kinds of action may therefore occur in the same organ, one or the other predominating at different times. This was found to be the case with horse liver, formation predominating at first, destruction later. With human kidneys, taken twelve to fifteen hours after death, 92-98 per

cent of the added urates were destroyed. Of course, in these experiments bacterial action was not excluded, but with the perfectly fresh and aseptic kidneys of herbivora 80-98 per cent of the urates were destroyed, while with the fresh kidneys of dogs only 14 to 19 per cent. During these experiments the formation of glyoxylic acid was observed in several instances, and this fact led to the suggestion of the following explanation of the mechanism of the action: The uric acid is first supposed to yield allantoin, and it is known that the elimination of allantoin is increased in cats and dogs after intravenous injection of urates. The allantoin is then hydrolysed to urea and glyoxylic acid,

according to the equation:
$$\text{HN} \begin{array}{c} \text{CO.NH} \\ | \\ \text{CO.CH.NH.CO.NH}_2 \end{array} + 2\text{H}_2\text{O} = 2\text{H}_2\text{N} \cdot \text{CO.NH}_2 + \text{CHO.COOH}.$$
 Glyoxylic acid and urea also easily condense to allantoin *in vitro*, by the reverse reaction.

By what method the large proportion of ammonia met with in the urine, with a protein-poor diet, is protected from conversion into urea is not known. A plausible explanation would be that the ammonia combines with sulfuric or phosphoric acid, produced during increased metabolism of tissue proteins, by oxidation of their sulfur and phosphorus, to form salts which are not convertible into urea. But this view finds no support in the metabolism experiments above cited, in which mineral sulfates and phosphates diminished in amount with increasing percentage of ammonia, while ester sulfates were increased in proportion to both mineral sulfates and total sulfur.

Although countless so-called determinations of urea have been made, very little is known of the actual quantities of urea present in the urine, and still less of its varying relations to other nitrogenous constituents, and to the total nitrogen, under different conditions of health and disease, because almost all of the processes which have been used, including all of the "clinical" processes, lead to erroneous results. Practically the whole of the literature upon this subject must be recast in the light of new investigations, made with more accurate methods.

About Quantitative Processes.—It would appear that enough has been said up to this point about quantitative methods of analysis of urine, and of their results, to warrant the advice to the practicing physician that he should abstain entirely from any attempt to use them, unless, indeed, he may spare the time from his practice to become a worker in a chemical laboratory. The perfection of methods has involved, as a necessity, increases in their complexity and time-consuming power, which have placed them entirely beyond the reach of the busy clinician. And, as for so-called "clinical processes," which waste time while pretending to save it (for any time spent in acquiring results confessedly inaccurate must be counted as wasted),

medical literature is loaded down with their product—a worse than worthless mass of rubbish.

Let the medical practitioner confine his activities in “urinalysis” to qualitative examinations for abnormal constituents, which are for the most part entirely within his capacity; but where quantitative determinations are required for any purpose, let them be made by an expert, competent to judge of the reliability of methods, and abreast of the time in their perfection. In this matter the general practitioner stands as much in need of the aid of a specialist, as he does of that of a skilful surgeon for a delicate operation. And in this connection it should also be said that the value of such investigations frequently depends upon comparisons of intake with output, and that in such cases the enquiry should not be entered upon unless the patient is willing to undergo the personal discomfort of a regulated and measured diet. Further, in such cases the fæces should also be submitted to analysis. In order that comparable quantitative results may be obtained at all, the following precautions are essential in

The Collection of Samples.—(1) The urine should be collected without admixture of any other solid or liquid substance whatever, except that, in hot weather, two or three drops of formalin may be placed in the bottle to prevent decomposition.

(2) It should be placed, *immediately after having been voided*, in a perfectly clean bottle or bottles. A half-gallon so-called mineral water bottle (Poland, etc.) is of sufficient capacity usually, and serves very well, as its original contents consisted of quite pure water.

(3) This receiver must be kept corked and cool, or preferably cold. If this precaution be neglected quantitative determinations of ammonia and of urea cannot be accurately made.

(4) The sample must be the entire urine of twenty-four hours. *No quantitative determination made with a sample not taken from the mixed and measured urine of twenty-four hours is of any value whatever.* The bladder is to be emptied when the collection begins, conveniently at 8 A.M., and this urine thrown away. All urine passed during the following twenty-four hours, including that obtained by emptying the bladder at 8 A.M. the next day, is to be collected.

For qualitative testing a sample may be taken at any time, and in any quantity, so it be sufficient. But as there are hourly variations in the elimination of all abnormal constituents, sometimes extending to complete disappearance, it is preferable to examine two samples, one taken in the morning, when the elimination is at the minimum, and the other at about three to four hours after the principal meal, for the maximum.

Quantitative Determination of Urea.—*Folin's Method.*—This method is based upon the decomposition of urea at 150° into ammonia

and cyanuric acid (p.404), and the decomposition of cyanuric acid by boiling alkaline solutions into ammonia and carbon dioxide (p. 396). Urea is calculated from the ammonia produced. To conduct the process 3 cc. of urine are placed in 200 cc. Erlenmeyer flask with 2 cc. of concentrated HCl (sp. gr. 1.14), and 20 gms. of crystallized $MgCl_2$ (the b. p. of which is about 160°), a small piece of paraffin is added to prevent frothing, and the flask is fitted with a return condenser, having three bulbs. The contents of the flask are heated to active boiling for about ten minutes, to expel the excess of water (which is recognized by drops from the condenser producing a hissing sound on falling back). The heat is then reduced to moderate boiling, which is continued for forty-five to sixty minutes. Water is then cautiously added to the still hot contents of the flask, at first guttatum, which are then transferred to a 1000 cc. flask, and diluted to 500 cc. with water. After addition of a little talcum powder and 7 to 8 cc. of 20 per cent NaHO solution, the ammonia is distilled off into N/10 acid, the distillation being continued for sixty to seventy minutes, after which the CO_2 which has collected in the acid is boiled out, and the NH_3 determined by titration as usual. It is essential to the accuracy of the results that during the heating an excess of acid be present, for which reason the condenser cannot be dispensed with, and that the heating and distillation be continued for the periods mentioned, to insure complete decomposition. Two corrections are required. Commercial $MgCl_2$ always contains NH_3 . Its tenure in this for 20 gms. must be determined and subtracted from the result. A separate determination of the ammonia in the urine must be made, and the number of cc. of N/10 NH_3 for 3 cc. corresponding thereto must also be subtracted. After these corrections have been made each cc. of N/10 NH_3 represents 0.1002 urea in 100 cc. No ammonia is given off in this process from uric acid, hippuric acid, creatinin, creatin or amido acids. The results are therefore accurate with proper manipulation. A suitably adjusted electric heater is very convenient, and with it the process may be conducted with little more attention than is required for an ordinary Kjeldahl. This process is recommended as the best yet devised, and it is difficult to see in what direction it can be improved upon, unless there be found to be some slight error due to components of the "undetermined nitrogen." In place of applying the process directly to the urine, it may be applied to the filtrates from the Mörner-Sjöqvist or Pflüger-Gumlich methods.

Mörner-Sjöqvist Method.—This method is based upon the fact that urea is not precipitated from its aqueous solution containing $BaCl_2$ and BaH_2O_2 by alcohol-ether, whereas the other nitrogenous constituents are so precipitated, except ammonia, hippuric acid, creatinin and traces of allantoin. To conduct the process: To 5 cc. of the

urine in a flask add 5 cc. of a saturated solution of BaCl_2 , containing 5 per cent of BaH_2O_2 , and 100 cc. of a mixture of two parts of 97 per cent alcohol and one part of ether, and allow the mixture to stand in a closed flask for twelve hours. The liquid is then filtered off, the precipitate washed with alcohol-ether, and the filtrate and washings distilled at about 55° (not above 60°). When the liquid has been reduced to about 25 cc., a little water and some MgO are added, and the evaporation continued until the liquid is reduced to 10 to 15 cc. The liquid is then transferred to a Kjeldahl flask with a little water, concentrated over the water-bath, and in it the ammonia is determined by the Kjeldahl method. -

Pflüger-Gumlich Method—differs from the preceding in that the nitrogenous constituents other than urea are precipitated out by phosphotungstic acid, and the nitrogen is determined in the filtrate by the Kjeldahl method. The Folin process is to be preferred to either the Mörner-Sjöqvist or Pflüger-Gumlich.

The least objectionable of the clinical processes will now be referred to, although, from what has been said above, it is clear that their use is not recommended:

Probably the most satisfactory process in the hands of the practitioner is that of Hüfner, based upon the reaction, to which attention was first called by Knop, of the alkaline hypobromites upon urea (p. 404), using, however, Dietrich's apparatus, or the more simple modification suggested by Rumpf, in place of that of Hüfner. The apparatus (Fig. 44) consists of a burette of 30-50 cc. capacity, immersed in a tall glass cylinder filled with water, and supported in such a way as to admit of being raised or lowered at pleasure. The upper end of the burette communicates with the evolution bottle *a*, which has a capacity of 75 cc., by means of a rubber tube.

The reagent required is made as follows: 27 cc. of a solution of caustic soda, made by dissolving 100 grams NaHO in 250 cc. H_2O , are brought into a stoppered, graduated cylinder, 2.5 cc. bromin are added, the mixture shaken, and diluted with water to 150 cc. The caustic soda solution may be kept in a bottle having a rubber stopper, but the mixture must be made up as required, a fact which, owing to the irritating



FIG. 44.

character of the bromin vapor, renders the use of this reagent in a physician's office somewhat troublesome. The bromin is best measured by a pipette of suitable size, having a compressible rubber ball at the upper end.

To conduct a determination, about 20 cc. of the hypobromite solution are placed in the bottle *a*; 5 cc. of the urine to be examined are placed in the short test-tube, which is then introduced into the position shown in the figure, care being had that no urine escapes. The cork, with its fittings, is then introduced, the pinchcock *b* opened, and closed again when the level of the liquid in the burette is the same as that in the cylinder. The decomposing vessel *a* is then inclined so that the urine and hypobromite solution mix; the decomposition begins at once, and the evolved N passes into the burette, which is raised from time to time, so as to keep the external and internal levels of water about equal; the CO₂ formed is retained by the soda solution. In about half an hour (the decomposition is usually complete in ten minutes, but it is well to wait half an hour) the height is so adjusted that the inner and outer levels of water are exactly even, and the graduation is read, while the standing of the barometer and thermometer are noted at the same time.

In calculating the percentage of urea from the volume of N obtained, it is essential that a correction should be made for differences of temperature and pressure, without which the result from an ordinary sample of urine may be vitiated by an error of 10 per cent. If, however, the temperature and barometric pressure have been noted, the correction is readily made by the use of the table (see Appendix B, III), computed by Dietrich, giving the weight of 1 cc. N at different temperatures and pressures.

In the square of the table in which the horizontal line of the observed temperature crosses the vertical line of the observed barometric pressure will be found the weight, in milligrams, of a cc. of N; this, multiplied by the observed volume of N, gives the weight of N produced by the decomposition of the urea contained in 5 cc. urine. But as 60 parts urea yield 28 parts N, the weight of N, multiplied by 2.143, gives the weight of urea in milligrams in 5 cc. urine. This quantity, multiplied by twice the amount of urine in 24 hours, and divided by 10,000, gives the amount of urea eliminated in 24 hours in grams. If the result be desired in grains the amount in grams is multiplied by 15.432.

Example.—Five cc. urine decomposed; barometer = 736 mm.; thermometer = 10°; burette reading before decomposition = 64.2; same after decomposition = 32.6; cc. N collected = 31.6. From the table 1 cc. N at 10° and 736 mm. BP weighs 1.1593. The patient passes 1500 cc. urine in 24 hours:

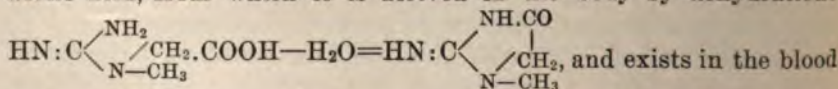
$$\begin{aligned}
 31.6 \times 1.1593 &= 36.6339 = \text{milligr. N in 5 cc. urine.} \\
 36.6339 \times 2.14 &= 78.3965 = \text{milligr. urea in 5 cc. urine.} \\
 \frac{78.3965 \times 3000}{10,000} &= 23.519 = \text{grams urea in 24 hours.}
 \end{aligned}$$

$$23.519 \times 15.432 = 362.94 = \text{grains urea in 24 hours.}$$

In using this process it is well to have the urea solution as near the strength of one per cent as possible; therefore if the urine be concentrated, it should be diluted. Even when carefully conducted, the process is not accurate; creatinin and uric acid are also decomposed with liberation of N, thus causing a plus error; on the other hand, a minus error is caused by the fact that in the decomposition of urea by the hypobromite, the theoretical result is never obtained within about eight per cent in urine. These errors may be rectified to some extent by multiplying the result by 1.044.

A process which does not yield as accurate results as the preceding, but which is more easy of application, is that of Fowler, based upon the loss of sp. gr. of the urine after the decomposition of its urea by hypochlorite. To apply this method the sp. gr. of the urine is carefully determined, as well as that of the liq. sodæ chlorinatæ (Squibb's). One volume of the urine is then mixed with exactly seven volumes of the liq. sod. chlor., and, after the first violence of the reaction has subsided, the mixture is shaken from time to time during an hour, when the decomposition is complete; the sp. gr. of the mixture is then determined. As the reaction begins instantaneously when the urine and reagent are mixed, the sp. gr. of the mixture must be calculated by adding together once the sp. gr. of the urine and seven times the sp. gr. of the liq. sod. chlor., and dividing the sum by 8. From the quotient so obtained the sp. gr. of the mixture after decomposition is subtracted; every degree of loss in sp. gr. indicates 0.7791 gram of urea in 100 cc. of urine. The sp. gr. determinations must all be made at the same temperature; and that of the mixture only when the evolution of gas has ceased entirely.

Creatinin (p. 389)—is the lactam of creatin, or methyl-guanidin acetic acid, from which it is derived in the body by dehydration:



and urine of adults, and in traces in milk, although it is absent in the urine of nursing infants. The quantity eliminated is from three to six times that of uric acid, 1.2 to 2.1 in twenty-four hours. The amount eliminated by a given individual is remarkably constant, and averages 6 per cent of the total nitrogen. With diminution of protein metabolism there is very little change in the absolute elimination of

creatinin, and therefore, by deminition of urea elimination, the relative value of the creatinin nitrogen increases so that, from furnishing only 3.4 per cent of the total nitrogen, it comes to furnish over 17 per cent. Although constant for a given individual, the absolute creatinin elimination varies with different persons, and seems to bear a relation to the body weight and to the degree of corpulence, in such manner that fat persons eliminate about 20 mgm. per kilo of body weight, and lean persons about 25 mgm. per kilo.

Creatinin seems, therefore, to be a product of tissue protein metabolism essentially (See Uric Acid, p. 721). Creatin is certainly produced in muscular tissue, and is dehydrated to creatinin in the system, and the elimination of the latter is increased with active muscular effort. In diseases attended with increased muscular activity there is both increase in the absolute elimination of creatinin, and increase in the percentage of its nitrogen in the total nitrogen. In rapid muscular atrophy, however, the creatinin elimination remains normal, or is slightly increased. In convalescence after illness of long duration the elimination of creatinin is greater with a meat diet than with other diets.

Formerly the only available method of **quantitative determination of creatinin** was a laborious process in which it was separated as its crystalline compound with ZnCl_2 , and its quantity calculated from that of the zinc oxid obtained therefrom. The *colorimetric process of Folin* is more accurate, and is rapidly conducted. It depends upon Jaffé's reaction, which consists of the formation of an intense red color when picric acid and a few drops of KHO or NaHO solution are added to a solution of creatinin, which becomes an orange color, similar to that of potassium dichromate solution, on dilution. The only other substances which may be present in the urine which give a similar color are acetone and acetoacetic acid and ester, which are pathological products, easily removable. The comparison solution is a N/12 solution of $\text{K}_2\text{Cr}_2\text{O}_7$, containing 24.54 gms. per liter. One tube of a colorimeter capable of adjustment to 0.1 mm. is filled to the depth of exactly 8 mm. with this solution. For comparison, 10 cc. of the urine are placed in a 500 cc. measuring flask, 15 cc. of a 1.2 per cent aqueous solution of picric acid, and 5 cc. of a 10 per cent NaHO solution are added, the mixture shaken and allowed to stand five minutes, after which it is diluted with water to 500 cc., and well mixed. The second tube of the colorimeter is rinsed out with this liquid, which is then run into the second tube to colorimetric equality with the first tube. Some previous practice with the dichromate solution in both tubes is necessary to train the eye to perception of equality of tint. The mean of three or four readings is taken, and with this the creatinin content in mgms. per 10 cc. of urine is calculated by the

formula $\frac{8.1}{x} \times 10$, in which x is the reading of the colorimeter. For example, if the mean of the readings be 7.2, then $\frac{8.1}{7.2} \times 10 = 11.25$ mgms. creatinin in 10 cc. urine. If the colorimetric value be less than 5 mm. the determination is to be repeated, using 5 cc. of urine in place of 10; and if the value be greater than 13 mm., with 20 cc. of urine in place of 10.

The question whether the urine contains **creatin** as well as creatinin, previously unanswerable, was solved by this process. It was found that, by heating 5 to 10 mgms. of creatin with 10 cc. H_2O and 5 cc. normal HCl on the water-bath for three hours, the creatin was quantitatively converted into creatinin. Therefore, by making two determinations by the above method, one with the urine directly, the second with the urine after four hours' heating under the above conditions, any creatin present would cause a higher value of the second determination, and the quantity of creatin may be determined from the difference between the two readings: 1 mgm. creatinin = 1.16 mgm. creatin. It was found that creatin is neither constantly present nor constantly absent, that some samples contain no creatin, and that in others its amount may rise as high as 1.16 mgm. in 10 cc. for 19.8 of creatinin also present. It was found also that in some urines a small fraction of creatinin is converted into creatin when the urine is allowed to stand for some days aseptically.

Uric Acid (p. 528)—is present in the urine of man and of the carnivora, and is particularly abundant in the solid urine of birds and reptiles, which consists almost entirely of ammonium urate. In the urine of the herbivora it exists only in traces, being replaced by hippuric acid.

We have seen (p. 733) that the former consideration of uric acid as an important intermediate substance in the formation of urea in mammals is no longer entertained. In reptiles nitrogen is almost exclusively eliminated as uric acid, and, as metabolism is extremely slow in these animals, this was held as strong argument in favor of the view that uric acid is a lower condition of oxidation of proteins, in the line of urea formation. But the force of this argument is lost in the light of the fact that in birds, in which metabolism is very rapid, the greater part of the nitrogen is also eliminated as uric acid. In reptiles and birds, therefore, uric acid cannot have that subordinate interest in the metabolism of proteins, other than nucleoproteids, that it is believed to have in mammals. It is true that both reptiles and birds excrete urea, but it is in such small amount that in general protein metabolism in these animals it occupies a position subordinate to uric acid. It has been observed that the same causes which produce increased urea elimination in mammals, such as the administration of

ammonium compounds, cause increased uric acid elimination in birds. That uric acid formation in birds depends upon an action of the liver is shown by the fact that geese, which normally eliminate about 60 to 70 per cent of the total nitrogen as uric acid, this percentage falls to 3 or 4 per cent after extirpation of the liver, an operation which these animals survive for about twenty hours. It may be supposed, therefore, that in birds uric acid may be formed in the liver from urea, or suitable ammonium compounds, by a so-called synthesis similar to that by which urea is formed in mammals from the same materials (p. 685). Indeed, it has been demonstrated that uric acid is formed from ammonia and lactic acid in the livers of birds, and lactic acid, known to be produced quite constantly in animal organisms, may have its origin in deamidation of alanin: $\text{CH}_3\text{CHNH}_2\text{COOH} + \text{H}_2\text{O} = \text{CH}_3\text{CHOHCOOH} + \text{NH}_3$. It is quite possible that both processes take place in the livers of both birds and mammals, the formation of uric acid predominating largely in the former, and that of urea in the latter.

That the predominating origin of uric acid and of the xanthin bases in mammals is from the purin bases of the nucleoproteids is, however, now conceded. Administration of nucleoproteids or of purin bases is followed by increased uric acid elimination, as is also the addition of food rich in purin bases, such as meat, liver, thymus, etc., to a fixed diet. In leukaemia, in which there is extensive destruction of the purin-rich leucocytes, the elimination of uric acid is above the normal. With a diet from which purin bases are entirely excluded the elimination of uric acid is greatly diminished, but never to complete extinction. There is therefore an "endogenous" origin of uric acid, i. e., from the tissue proteins, as well as an "exogenous" origin, i. e., from the circulating proteins. The quantity of exogenous uric acid eliminated varies, of course, with the purin content of the food; that of the endogenous uric acid, although varying with different individuals, is quite constant with the same individual, when the diet, although purin-free, contains a sufficient supply of protein. The daily elimination of endogenous uric acid under these conditions varies with different individuals from 0.3 to 0.6 gm. But with a diet which is both purin-free and also nitrogen-poor, the elimination of endogenous uric acid is markedly diminished as the total nitrogen elimination is reduced, but not proportionately to such reduction. Thus in a normal individual eliminating 0.55, 0.53, and 0.53 gm. of uric acid, with 13.4, 13.9, and 16.8 gms. of total urine nitrogen in three consecutive days upon a purin-free and nitrogen-sufficient (19 gm. N in twenty-four hours) diet, the elimination fell to 0.34, 0.29, 0.32, 0.26 0.28, and 0.26 in six days, with 7.5, 6.7, 4.4, 5.3, 4.8, and 3.6 of total nitrogen, upon a diet containing but 1 gm. nitrogen per

diem. Under these circumstances there is not the same degree of constancy of elimination as in the case of creatinin (p. 719). The endogenous uric acid represents the extent of cell work of the individual, to which is added the exogenous uric acid, varying in amount with the degree of richness of the food in xanthin bases. It is not to be inferred that the portions of substance derived from these two origins are kept distinct in their transit towards excretion, but rather that there exists a dynamic equilibrium between them, as between a liquid and its saturated vapor (p. 30), and that that which is exogenous material at one instant may become endogenous the next, and *vice versa*.

From what has been said in that connection in discussing urea, it appears to be certain that not all of the uric acid which is formed in the economy is eliminated by the kidneys. A portion is destroyed in the system, and that which is eliminated is merely the residuum which has escaped conversion. This is further proven by experiments upon rabbits, by which it was shown that only 18 per cent, or less, of uric acid, dissolved by piperazin, injected into the circulation could be recovered in the urine; and the fraction was still smaller when the administration was by the mouth, possibly because of destruction in the liver.

With a sufficient, purin-free, mixed diet the daily elimination of uric acid by a healthy man is from 0.3 to 0.6 gm.; with a purin-rich diet it may rise to 1.5 or 2.0 gms.; and with a nitrogen-poor diet it may fall as low as 0.22 gm. In relation to total nitrogen its nitrogen may be 0.7 to 1.4 per cent of the total with a mixed diet, and 0.8 to 4.0 with one which is nitrogen-poor.

The results of quantitative determinations in pathological conditions are somewhat conflicting, and those obtained by the older methods are for the most part erroneous, being affected with a minus error. The following facts may, however, be considered as established: In leukæmia there is both absolute and relative increase, the absolute amount being from 1 to 5 gm. in 24 hours, and the proportion to urea increased to 1:45 to 1:12. A similar increase occurs in splenic diseases, and in hepatic cirrhosis. In gout there is diminished elimination during the chronic period, most marked just preceding an attack, and an increased elimination during and following the exacerbations. In acute articular rheumatism the elimination increases, to return to and fall below the normal during convalescence. In diabetes the amount of uric acid is usually subnormal, although it is often increased to as high as 3 gm. in 24 hours, when the sugar is diminished in quantity. By reason of its very sparing solubility, uric acid frequently forms sediments and calculi, consisting either of free uric acid or of the less soluble of the urates. It must be noted in this connection that uric acid is much

more soluble in the presence of urea than in pure water. While 36,000 parts of water are required to dissolve 1 part of uric acid, the same quantity dissolves in 1900 parts of a 2% solution of urea, about the proportion contained in the urine.

The principal methods of quantitative determination of uric acid are those of Heintz, of Hopkins and the Ludwig-Salkowski method. The older *method of Heintz*, which consists in precipitation of the uric acid by strong acidulation with hydrochloric acid, and weighing the crystals, is inaccurate by reason of incomplete precipitation by this treatment; indeed, samples are met with from which no precipitation whatever occurs.

Hopkins' method is but slightly more elaborate than Heintz's, but much more reliable: 100 cc. of urine are saturated with powdered ammonium chlorid (for which about 30 gm. are required), and the solution mixed and allowed to stand 2 to 3 hours with occasional stirring. By this treatment the uric acid is almost completely precipitated as acid ammonium urate. The precipitate is collected on a filter, washed with saturated NH_4Cl solution, and dissolved in the smallest possible quantity of hot water. To this solution 5 cc. of HCl (1:3) are added, and the mixture evaporated on the water bath until crystals of uric acid begin to form. These are collected upon a small, weighed filter, washed successively with water, alcohol and ether, dried and weighed. A correction is necessary for the slight solubility of uric acid, which is made by adding 0.045 mgm. for each cc. of water used in the final washing.

In a modification, the chief object of which is to remove other reducing substances precipitated with ammonium urate, and thus permit of titration with permanganate, and known as the *Folin-Shaffer Method*, 200 cc. of urine are measured into a tall beaker and 50 cc. of a reagent made by dissolving 500 gms. of ammonium sulfate, 5 gms. of uranium acetate, and 60 cc. of 10 per cent acetic acid in 650 cc. of water, and making up to one liter. The mixture of urine and reagent is allowed to stand without stirring for about half an hour, after which the clear liquid is decanted off, or filtered through a double folded filter. To 125 cc. of the clear liquid 5 cc. of strong ammonia are added, and the mixture set aside until next day. The precipitate is then collected upon a filter, and washed with 10 per cent ammonium sulfate solution until the filtrate is almost or quite free from chlorids. The precipitate is then rinsed back into the beaker; enough water is added to make 100 cc., the precipitate is dissolved by addition of 15 cc. of concentrated H_2SO_4 , and the solution at once titrated with N/20 potassium permanganate solution, each cc. of which corresponds to 3.75 mgm. of uric acid. A correction of 3 mgm., for the solubility of the ammonium urate in the volume of liquid used, is to be added to the result.

The *Ludwig-Salkowski Method*, if properly conducted, is probably somewhat more accurate, but it is more intricate, and requires to be rapidly completed to avoid error. It depends upon the precipitation of the uric acid as its silver salt, the decomposition of this by HCl, and the collection and weighing of the liberated uric acid. The student is referred to more comprehensive treatises for the details of the process.

Xanthin Bases—(p. 531).—The occurrence of guanin and of carnin in the urine has not been demonstrated; and of the remaining xanthin bases which are met with in the urine the most abundant are heteroxanthin, paraxanthin, and 1-monomethyl-xanthin. They are normally present in small amount only, the total elimination being from 15 to 45 mgm. in 24 hours. They undoubtedly originate in the metabolism of the nucleoproteids, and are increased in amount after administration of nucleins, and in conditions attended with increased metabolism of leucocytes. They may also originate from the caffeine and theobromin contained in coffee, tea and cocoa (p. 533). Xanthin occasionally forms vesical calculi of considerable size. Their quantitative determination is best effected by Salkowski's method, based upon precipitation of their silver compounds.

Hippuric Acid—(p. 479)—is an aromatic amido-acid, benzoyl-amido acetic acid, which exists in greatest abundance in the urine of the herbivora, and only in small amount in normal human urine, although the daily elimination varies within quite wide limits, 0.29 to 2.84 gm., and is still further increased when benzoic acid, cinnamic acid or substances containing those acids or their compounds are taken.

Hippuric acid may be considered as formed by the substitution of the radical, benzoyl, of benzoic acid for a hydrogen atom in the amido group of amido-acetic acid: $C_6H_5.CO.OH + CH_2.NH_2.COOH = H_2O + CH_2.NH(C_6H_5.CO).COOH$; its production in the body, therefore, involves the formation of glycocoll and of an aromatic derivative which may supply the benzoyl factor. Both of the constituents of hippuric acid result, undoubtedly, from protein metabolism. Glycocoll is a well-recognized product of such action, but the method and seat of production of the benzoyl radical are not so clear. Benzoyl-propionic acid, $CH_2(C_6H_5.CO).CH_2.COOH$, is known to be a product of intestinal putrefaction; and that this is capable of yielding the benzoyl radical is demonstrated by the fact that when it is injected into the circulation it is eliminated as hippuric acid. The administration of benzoic acid is also followed by a corresponding increase in the elimination of hippuric acid. That some of the steps in the formation of hippuric acid are the result of intestinal putrefaction is also indicated by marked diminution in its elimination in dogs

whose intestines are disinfected. It is probable, also, that the final steps occur in the kidney, as hippuric acid is formed when arterial blood containing glycocoll and benzoic acid is passed through the isolated kidneys of dogs.

Little is known of the variations in elimination of hippuric acid in pathological conditions.

Oxaluric Acid—(p. 408)—is a monureid, $(\text{CON}_2\text{H}_3)\text{CO}\cdot\text{COOH}$, which exists in the urine as its ammonium salt in very small amount. It is readily decomposed, even by boiling its solution, into urea and oxalic acid, and it is undoubtedly concerned in the formation of the oxalates of the urine.

Allantoïn—(pp. 515, 713)—is a diureid which occurs in very minute quantity in the urine of adults, in somewhat larger amount in that of pregnant women, and in that of infants during the first eight days of life, when the quantity of urea is very small. It is increased in the urine of dogs after administration of uric acid, and is, possibly, produced from this in the economy.

Urinary Pigments and Chromogens.—The yellow color of the urine is due to the presence of more than one coloring-matter. The most abundant of those constantly present is **urochrom**, which is accompanied by small quantities of hæmatoporphyrin (p. 665), and by a chromogen, **urobilinogen**, which, shortly after the urine is voided, gives rise to the coloring-matter, **urobilin**. Besides these and the indoxyl- and skatoxyl-compounds, the urine frequently contains a red coloring-matter, **uroerythrin**, which is, however, not constantly present. A number of urinary coloring-matters have been named, which are probably among the above-mentioned or products of the action of acids or of other reagents upon them or upon other constituents of the urine.

Urochrom (of Garrod)—is closely related to urobilin, from which it differs in not being precipitated by saturation of its solution with ammonium sulfate, and in not giving either the spectrum or the fluorescence of urobilin. The two substances are readily converted one into the other; urochrom into urobilin by the reducing action of aldehyde, and urobilin into urochrom by moderate oxidation with permanganate. Urochrom contains nitrogen, but no iron; it is amorphous, brown, soluble in water and in dilute alcohol, sparingly soluble in strong alcohol, amylic alcohol or acetic ether, insoluble in ether, chloroform or benzene. It is precipitated by lead acetate, silver nitrate, or mercuric acetate.

Urobilin (of Jaffé)—does not exist in fresh urine, but is formed from urobilinogen, probably by the action of light. There are some differences in the properties of urobilins, as described by different observers, and there may be several urobilins, or **urobilinoids**, nor-

mal, febrile, etc. Urobilin-like substances have also been obtained from bilirubin, from hæmatin and from hæmatoporphyrin, and, as they have been formed both by reduction and by oxidation, they cannot be identical with each other. Urobilin is apparently identical with the stercobilin of the fæces, which is formed in the intestine from the bile-pigments. Both the urinary and the fæcal pigment are increased in amount with increased intestinal putrefaction.

Urobilin is amorphous, reddish-brown to reddish-yellow, soluble in alcohol, amylic alcohol and chloroform, less soluble in ether, sparingly soluble in water, in which its solubility is increased by the presence of neutral salts. It is precipitated completely from its solutions by saturation with ammonium sulfate after addition of sulfuric acid. It is soluble in alkalies, from which solutions it is precipitated by acids. It is precipitated from neutral or faintly alkaline solutions by lead acetate, and by zinc sulfate, but not by mercuric salts. It does not give the Gmelin reaction, but gives a reaction similar to the biuret reaction. Its concentrated, neutral, alcoholic solutions are brown in color; the dilute solutions yellow or rose-colored, and showing a strong green fluorescence. The acid solutions have the same colors, are not fluorescent, but show a faint absorption band between b and F. If zinc chlorid be added to the ammoniacal solution it becomes red, and shows a fine green fluorescence. This solution gives a broad absorption band, extending from about midway between E and b very nearly to F; and, if concentrated, a second band over E appears on careful acidulation with sulfuric acid.

The chromogen, **urobilinogen**, is a colorless substance, which may be obtained by precipitation, caused by saturation of the urine with ammonium sulfate; or may be extracted from the urine, acidulated with acetic acid, by agitation with acetic ether. It is soluble in chloroform, ether and amylic alcohol. Its solutions give no spectrum, and, on exposure to light, soon become colored, from conversion of the urobilinogen into urobilin.

The quantity of urobilin eliminated in 24 hours has been variously estimated as from 30 to 140 mgm. Hoppe-Seyler's method of determination consists in acidulating 100 cc. of urine with H_2SO_4 , precipitating by saturation with $(\text{NH}_4)_2\text{SO}_4$, collection of the precipitate after 24 hours, washing with saturated $(\text{NH}_4)_2\text{SO}_4$ solution, extraction of the residue with a mixture of equal parts of chloroform and alcohol, removal of alcohol by agitation of this, filtered, solution with water, evaporation of the chloroform solution in a weighed beaker, drying at 100° , washing the residue with ether, drying, and weighing. By this method Hoppe-Seyler found a mean of 123 mgm. in 24 hours, and extremes of 80 and 140 mgm. A spectrophoto-

metric method, based upon the same principle as those for hæmoglobin and for indican, also gives good results.

Pathologically the elimination of urobilinogen is increased in conditions involving increased metamorphosis of blood corpuscles, in fevers, and in icterus, in chronic lead poisoning, and in acute poisoning by antipyrin and antifebrin.

Uroerythrin exists in small quantity in normal urine, and is the substance which gives a pink or red color to "lateritious deposits." It is soluble in amylic alcohol, forming solutions which are rose-colored if dilute, orange or fiery-red if concentrated, which are not fluorescent, and which give a spectrum of a single band, broader than that of urobilin, extending from midway between D and E nearly to F, with a lighter part between E and b. Its solutions are colored carmine-red by H_2SO_4 , and grass-green by alkalis. A rough method for detecting its presence in excess consists of precipitating the urine with lead acetate, and allowing the precipitate to settle for 15 minutes in the dark. In presence of excess of uroerythrin the precipitate is distinctly pink, otherwise it is white.

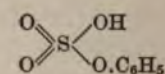
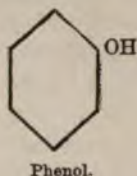
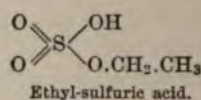
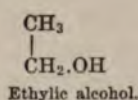
Uroerythrin is increased in amount in the urine after violent exercise, after excess of food or of alcohol, in disturbances of digestion, fevers, and derangements of the hepatic circulation.

Organic Compounds Containing Sulfur.—We have seen (p. 702) that the sulfur eliminated in the urine is contained in the three forms of mineral sulfates, ester sulfates and neutral sulfur. So far as is known, all of the sulfur compounds from which the neutral sulfur is derived also contain nitrogen. As practically all of the sulfur compounds of the urine are derived from the metabolism of the sulfur-containing complex of the proteins, attempts have been made to estimate variations in protein metabolism by determinations of total sulfur and of its several fractions in the urine. These have not been as satisfactory in their results as similar investigations based upon nitrogen determinations, principally because of the much smaller (0.3 to 2.4 per cent) and more varying sulfur content of the proteins, and partly because less reliance is to be placed upon the strict accuracy of sulfur determinations than upon those of nitrogen by existing methods.

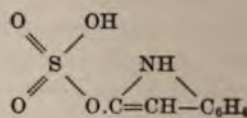
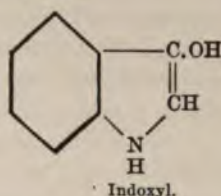
Certain regular variations of total sulfur and of its distribution have, however, been observed, dependent upon the protein content of the food. With diminution of protein metabolism there is, as would be expected, a marked diminution of the total sulfur elimination. Thus a healthy man, of 70 kilos weight, whose total urinary sulfur elimination during four days upon a mixed diet was 3.32, 3.09, 3.27 and 3.34 gms. SO_3 , excreted upon a nitrogen-poor diet 1.45, 1.05, 0.88, 0.65, 0.88 and 0.77 gms. This diminution in absolute amount fell principally upon the mineral sulfur, the ester sulfur being dimin-

ished to a much less degree and the neutral sulfur remaining almost constant, and consequently the percentage of mineral sulfur was diminished, while those of both ester-sulfur and neutral-sulfur were increased.

Ester-sulfates.—The occurrence of these compounds has been referred to in connection with the sulfates (p. 702), and they are considered here at greater length, as the most important among them contain nitrogen. Their constitution is similar to that of the acid esters (p. 358), from which they differ in containing phenolic in place of alcoholic radicals. Their relations are shown by the following formulæ:



Phenyl-sulfuric acid.



Indoxyl-sulfuric acid.

The compounds of this class which are known to occur in the urine are the sodium and potassium salts, particularly the latter, of the ester-sulfuric acids of phenol, para-cresol, catechol, quinol, indoxyl, and skatoxyl.

The phenol and para-cresol compounds are usually determined together by precipitation with bromin water, by a method which is not very accurate, and which determines not only the phenols in this form of combination, but also that existing in phenyl-glucuronic acid. By this method the amount of phenol and para-cresol eliminated has been found to vary from 17 to 51 mgm. in twenty-four hours. They have not the poisonous qualities of the phenols from which they are derived, and their formation serves to protect the system not only from the toxic effects of these substances, when formed as products of intestinal putrefaction, but also from that of carboic acid to the limit of the amount of sulfates available. In poisoning by carboic acid the whole of the sulfuric acid of the urine is in ethereal combination.

Of the three diphenols, catechol and quinol have been found in the urine of the horse, and in traces in human urine. The third, resorcinol, has not been met with in this situation.

Indoxyl-sulfates — Indican — Uroxanthin — (p. 541) is the principal parent substance of urinary indigo, which is also derived from indoxyl-glucuronic acid. The origin of both is undoubtedly in the indole produced in intestinal putrefaction. They disappear from the urine of dogs whose intestines are disinfected, they are not present in the urine of new-born infants, and they were also absent in a case of artificial anus at the lower part of the ileum. On reduction of the protein content of the diet to the minimum they are very much reduced in amount, or disappear entirely, owing to lack of pabulum for the saprophytic bacteria in the intestine.

The amount of indigo derivable from the two compounds mentioned, eliminated in 24 hours, is from 5 to 20 mgm. normally in man. In some of the lower animals it is much greater, in the horse 25 times greater. It is nearer the higher limit with animal food, nearer the lower with a vegetable diet. The elimination of an excess is designated as *indicanuria*, and is a measure of the intensity of putrefactive changes taking place in the intestine. Therefore it occurs in *hypochlorhydria* (p. 619) from any cause. But in the opposite condition of *hyperchlorhydria* in gastric ulcer there is also *indicanuria*. *Indicanuria* also occurs in conditions in which there is diminished peristalsis of the small intestine, as in *ileus* and *peritonitis*, not in simple constipation; also in conditions in which putrefactive changes occur in the body elsewhere than in the intestine, as in *empyema*, *putrid bronchitis*, *gangrene of the lungs*, etc.

The tests used for the detection and quantitative estimation of indoxyl derivatives in the urine are based upon their decomposition by hydrochloric acid into indoxyl and sulfates, and the oxidation of the former to indigo blue.

Obermayer's modification of the *Jaffé* method is probably the best: The urine is mixed with 1/5 its volume of 20% solution of lead acetate and filtered. The filtrate is mixed with an equal volume of fuming hydrochloric acid containing 3:1000 of ferric chlorid, a few drops of chloroform are added, and the mixture strongly shaken 1 to 2 minutes. With normal urine the chloroform remains colorless or almost so; but if an excess of indoxyl compounds be present the chloroform is colored blue, and the depth of the color is a rough indication of the degree of the excess. An arbitrary expression of the quantity of indigo may be made by *Folin's* method of colorimetric comparison with *Fehling's* solution: Exactly $\frac{1}{100}$ of the total urine of twenty-four hours is taken for each determination. This is treated with *Obermayer's* reagent and the liberated indigo is taken up with

5 cc. of chloroform. This solution is compared with Fehling's solution in a colorimeter, the copper solution being given the arbitrary value of 100. Colorimetric comparisons of the solutions of indigo obtained from the urine with pure blue liquids are somewhat interfered with by the red color of the skatoxyl derivative which accompanies the former. The best method of more exact quantitative determination is Müller's spectrophotometric method, which is based upon the same principle as Vierordt's method of hæmoglobin determination (p. 676), and requires similar apparatus.

Skatoxyl-sulfates—Urohæmatin—correspond in constitution to the indoxyl-sulfates, and have a similar origin. Like the indoxyl compounds, they are chromogens, and on decomposition they yield red or violet coloring-matters, which are referred to as "indigo red." When the Obermayer test as above described, but before addition of chloroform, is applied to urine containing excess of skatoxyl compounds, it becomes red or violet in color, and chloroform when added and shaken with the liquid is colored red or violet. The "reaction of Rosenbach" is due to urohæmatin. It consists of the addition of concentrated nitric acid drop by drop to the boiling urine, which, in presence of excess of the chromogen urohæmatin, assumes a deep wine-red color, which is usually tinged blue from the presence of indigo blue. Such urines also turn darker, reddish, violet, or even black, from the surface downwards, on mere exposure to air.

Neutral Sulfur Compounds.—The absolute amount of neutral sulfur eliminated is not affected by the protein-content of the diet, varying from 0.10 to 0.35 gm. in twenty-four hours. Its proportion to total sulfur varies from 3.4 to 10.0 per cent with a mixed diet, and from 11.0 to 36.0 per cent with a nitrogen-poor diet.

But little is known definitely of the nature of the compounds from which this neutral sulfur is derived. A considerable proportion is contained in substances derived from the sulfur compounds of the bile, which in turn originate from the cystin complex of the proteins. Taurocarbamic acid, really a substituted urea: $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, and taurin, its acid component: $\text{H}_2\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, both exist in normal urine, but whether constantly or not is not determined. When taurin is administered to men or dogs it is eliminated partly in its own form and partly as ammonium taurocarbamate, the synthesis of the taurocarbamate from urea and taurin probably occurring in the kidneys.

Oxyproteic acid, alloxyproteic acid, and antoxyproteic acid are amorphous, solid substances, containing sulfur and nitrogen, which appear to be definite compounds, and which it is said are eliminated in quite notable quantity: 3 to 4 gms. daily. If the observations which have been published concerning them be verified, they may

account for a considerable proportion not only of the neutral sulfur, but also of the undetermined nitrogen. They are not proteins, as they do not give the xanthoproteic or biuret reactions, although oxyproteic acid gives a faint Millon reaction. They are extremely soluble and are separated from the urine only with considerable difficulty. Two other nitrogen-sulfur acids have been described as occurring in normal urine: **uroproteic acid** and **uroferric acid**, the former of which is probably identical with alloxypoteic acid, and the latter is a sulfo-conjugate acid.

A **thiocyanate** is constantly present in the urine of man and of many animals; in man to a daily elimination of 0.2 to 0.8 gm. It is probably the thiocyanate of the saliva and gastric juice. The so-called mucin which constitutes the organic portion of the "nubecula" which separates from the urine on standing is probably a nucleoproteid (see Cystin, etc., p. 757).

Organic Compounds Containing neither Nitrogen nor Sulfur.—These are few in number and are present only in small amount. The best known are oxalic acid and the conjugate glucuronates.

Oxalic Acid—is a normal constituent of the urine in small amount, not exceeding 0.02 gm. in 24 hours, and is present as calcium oxalate, held in solution by the acid reaction of the monosodic phosphate. It is partly taken in with the food, as it exists in many fruits and vegetables, apples, spinach, sorrel, asparagus, rhubarb, etc. But it is also produced in the system from proteins and fats, as it does not disappear from the urine when the diet is limited to these, or with deprivation of food. Calcium oxalate is frequently deposited from subacid urines either in octahedral crystals or in dumb-bells, and sometimes forms calculi, **mulberry calculi**, which are white, hard and nodulated. The elimination of oxalic acid is increased in intestinal disturbances, sometimes with transient albuminuria, and sometimes in diabetes. Idiopathic oxaluria, or the oxalic acid diathesis, is a condition in which the elimination of oxalates is notably increased, the cause of which is unknown. In oxalic acid poisoning the elimination of the poison takes place through the kidneys, and the tubules become plugged with crystals of calcium oxalate.

For the **quantitative determination of oxalic acid** 500 cc. of urine are treated with CaCl_2 , rendered alkaline with ammonium hydroxid, and then acid with acetic acid. In 24 hours the precipitate is collected upon a small filter, washed with water, and extracted with dilute hydrochloric acid (which leaves the uric acid upon the filter). The acid solution is again alkalized with ammonium hydroxid and the precipitate collected upon a small filter, washed, dried, burnt, strongly ignited and weighed as calcium oxalate.

weight of CaO found, multiplied by 2.2857, gives the amount of calcium oxalate; or, multiplied by 1.6071, the amount of oxalic acid in 500 cc. urine.

Conjugate Glucuronates.—Not all of the phenolic compounds, skatoxyl, indoxyl, phenol, etc., produced by intestinal putrefaction goes to form ester sulfates; a portion of each of these substances is constantly eliminated in the urine as compounds of glucuronic acid: $\text{CHO} \cdot (\text{CHOH})_4 \cdot \text{COOH}$. This acid does not occur in its own form, or in those of its simple salts or esters, in the urine or elsewhere in the system, but only in the shape of salts of conjugate acids which it forms with phenols and with a great variety of other compounds, both aliphatic and cyclic. These conjugate compounds appear to be glucosid-like substances (p. 465) in which the glucuronic acid residue is not contained in its own form, but from which it may be split by a simple decomposition attended by atomic rearrangement: $\text{C}_6\text{H}_5 \cdot \text{O} \cdot (\text{CHOH})_5 \cdot \text{COOH} = \text{C}_6\text{H}_5 \cdot \text{OH} + \text{CHO} \cdot (\text{CHOH})_4 \cdot \text{COOH}$. Indeed, a glucosid is known, called euxanthic acid, which yields glucuronic acid by such decomposition. That glucuronic acid does not exist in the system except in conjugate combination is probably not due solely to the fact that, because of its great proneness to oxidation, it can only exist there when so protected, but probably also to the method of its formation. The most natural origin of glucuronic acid would at first sight appear to be by oxidation of glucose: $\text{CHO} \cdot (\text{CHOH})_4 \cdot \text{CH}_2\text{OH}$, but it is not conceivable that the primary alcoholic group could be converted into a carboxyl, leaving the much more readily oxidizable aldehyde group intact; and no such formation has been realized *in vitro*. It is much more probable that glucuronic acid is not formed at all in the system, but that the glucosid-like substances above referred to are produced by actions between some carbohydrate and the phenolic or other compounds, and that glucuronic acid, or the simple glucuronates, are only produced in the decomposition. The normally formed conjugate glucuronates are present in the urine only in small amount, but after administration of certain medicinal substances these are eliminated in the form of their glucuronic derivatives, such as **campho-glucuronic acid** with camphor, and **urochloralic acid** with chloral. The conjugate glucuronic acids are lævogyrous, while the acid itself is dextrogyrous. They are readily hydrolysed by dilute acids, with liberation of glucuronic acid. Thus urochloralic acid is decomposed into glucuronic acid and trichlor-alcohol: $\text{CCl}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot (\text{CHOH})_4 \cdot \text{COOH} + \text{H}_2\text{O} = \text{CHO} \cdot (\text{CHOH})_4 \cdot \text{COOH} + \text{CCl}_3 \cdot \text{CH}_2\text{OH}$. Glucuronic acid is a syrup, but forms crystalline salts; it is very soluble in water and in alcohol; it reduces the salts of copper, silver and bismuth; is not fermentable, gives the furfural reaction, also the phloroglucin reaction of the pentoses, and forms a crystalline compound with phenylhydrazin.

Toxicity of Urine.—Human urine, when injected into the circulation of animals, is quite poisonous. Thus, rabbits are killed by an average amount of 45 cc. of normal human urine per kilo of weight of the animal, injected at one time. The urine of persons suffering from febrile diseases is more actively poisonous than that of healthy individuals. The urine excreted in the early morning hours is more active than that formed during the day and early night, and the night urine produces convulsions, while the day urine behaves as a narcotic poison. The urine of some of the lower animals, notably that of the cat, is still more poisonous to rabbits than human urine. The toxicity of the urine is referable in part to the action of the potassium salts (p. 229), but it is not proportionate to their quantity. It is estimated that about 45 per cent of the poisonous action is due to potassium compounds; the remainder being due in part to the urinary coloring-matters, in part to the moderately toxic quality of urea, uric acid, etc., and in part to the presence of urinary leucomains, so-called ptomains. Several observers have obtained minute quantities of basic, actively poisonous substances from normal urine, and in larger amount from febrile urine. The exact chemical nature of these bodies is not determined, although one of them, Pouchet's base, has been obtained in the crystalline form, and was found to have the composition $C_7H_{14}N_4O_2$, or $C_7H_{12}N_4O_2$. True ptomains, such as cadaverin, putrescin, and other diamins have also been found in pathological urines, notably in cystinuria.

ABNORMAL CONSTITUENTS.

Of the following substances some, such as albumin, hæmoglobin, etc., are literally abnormal to the urine, that is their presence in any amount is the result of a pathological condition; others, such as glucose, cystin, etc., are considered abnormal for reasons of convenience; they are normally present, but only in very minute quantities, insufficient to be revealed by the tests customarily used, but are much increased in amount in certain pathological conditions.

Proteins.—The proteins which may occur in the urine are serum albumin, serum globulin, albumoses, including Brücke's peptone, and histon, a nuclealbumen, fibrin, and hæmoglobin.

Serum Albumin and Serum Globulin — are usually included in the term "albumin," as clinically applied to the urine, as both respond to the tests generally used. The question whether albumin is or is not a strictly normal constituent of the urine, in the sense above indicated, has been much discussed. The weight of evidence is, however, in favor of the view that the presence of albumin is always an abnormal condition. That it may be present, however, in quantities as large as 25 to 75 mgm. to the litre, in the urine of

under conditions which are not absolutely pathological, although departing from those which are usual, cannot be denied.

Serum albumin and serum globulin appear in the urine in a great variety of abnormal conditions, usually in quantity not exceeding 5 p/m, rarely reaching 10 p/m, and very exceptionally 50 p/m. (1) *Functional albuminurias* include those conditions which are sometimes considered as so-called "physiologic," or normal albuminurias, in which the presence of albumin is transitory and due to an exaggeration or deficiency of some normal condition; after severe muscular exertion, under great mental strain or emotion, in anæmic children and youths, accompanying excessive elimination of uric or oxalic acid, alimentary albuminuria due to excess of protein diet, particularly if raw. (2) *Febrile*, in most acute febrile diseases, particularly during convalescence. In typhoid it is always present, and disappears on the fifth to the eighth day in light cases, on the tenth day or later in severe cases. In pneumonia albumin is always present, sometimes abundantly. In any acute febrile disease albumin may be present, without the existence of any structural change in the kidney. (3) *Circulatory*, due to disturbances of the blood-pressure, in which the quantity of albumin is usually small, as in valvular heart-lesions, degeneration of the heart muscle, diseases of the coronary arteries, impeded pulmonary circulation, in pregnancy by pressure upon the renal veins, after cold baths, in intestinal catarrh and in Asiatic cholera. (4) *Hæmic*, due to pathologic modification of the blood proteins, in purpura, scurvy, leukæmia, pernicious anæmia, jaundice, diabetes, and syphilis. (5) *Toxic*, by the action of hæmatic poisons such as lead, mercury, chloroform, or by irritating action upon the glandular epithelium of the kidney, such as is caused by mercury, cantharides, oxalic acid, mineral acids, iodine, phosphorus, arsenic, antimony, carbolic acid, salicylic acid, turpentine, and nitrates. (6) *Accidental*, by the presence in the urine of blood, pus, or semen. So far as the two former are concerned, they may be either renal, or post-renal in origin. (7) *Nephritic*, in acute nephritis albumin is present in large amount, as much as 5 to 20 gm. in 24 hours, and the sediment contains casts. In chronic parenchymatous nephritis albumin is also constantly present, and in still larger quantity, as high as 15 to 30 gm. in 24 hours. In chronic interstitial nephritis the amount is small, rarely exceeding 2 to 5 gm. in 24 hours, and variable, while casts may be absent. In amyloid degeneration the amount is usually small, although it may reach 10 gm. in 24 hours. In this condition the proportion of serum globulin to serum albumin is greater than in other kidney lesions, it is usually from 1:0.8 to 1:1.4. Pure globinuria, that is the presence in the urine of serum globulin, unaccompanied by serum albumin, has not been observed.

For the detection of serum albumin and serum globulin in the urine it must be perfectly clear. If not so it is to be filtered, and if this does not render it transparent, it is to be treated with a few drops of magnesia mixture (p. 168 note), and again filtered. Or the urine is shaken with kieselguhr (diatomaceous earth) and filtered.

(1) *Heat and nitric acid test*.—The clear urine, if alkaline, is rendered *just* acid by addition, guttatim, of dilute acetic acid (nitric acid should not be used, and the acidulation is imperative). The urine is now heated to near boiling, and if a cloudiness or coagulum be formed, nitric acid is added slowly to the extent of about ten drops. If heat produces a cloudiness which clears up completely on addition of nitric acid, it is due to excess of earthy phosphates. If a cloudiness caused by heat do not clear up (it may increase) on addition of nitric acid, it is due to serum albumin or serum globulin. Sometimes the urine after heating and addition of nitric acid deposits a granular sediment on cooling; this is due to the separation of urates.

(2) *Heller's test*—is more delicate than the above, and reacts with urine containing 0.002 per cent. of albumin. About 1 cm. of nitric acid is placed in a test-tube, which is then held at an angle and the urine is allowed to flow slowly from a pipette upon the surface of the acid (Fig. 45) so as to form a distinct layer with the minimum of mixing of the two liquids. The procedure frequently directed, of "underrunning" the acid from a pipette under the urine, placed in a test-tube, does not give as good results. After withdrawing the pipette, the test-tube is returned to the vertical slowly, and the line of junction of the two liquids examined against a dark background. If the urine contain albumin a white, opaque band, whose upper and lower borders are *sharply defined*, will be seen at the line of junction of the two liquids. A *colored band* is generally observed in applying this test, which has no relation to the presence



FIG. 45.

of albumin, it may be of some shade of red from the presence of excess of normal coloring matter, or, of uroerythrin, blue, or almost black, from the presence of indican in excess, or giving the colors of the Gmelin reaction (p. 637) in the presence

of bile. When urates are present in excess a white zone is also formed which, however, differs from that caused by coagulation of albumin in the following particulars: it is not at, but slightly above, the line of contact of the two liquids; while its lower border may be sharply

defined, it has no upper border, but shades off gradually in the upper layer; and it is not produced with the urine diluted with one or two volumes of water. When urea is present in excess, crystals of urea nitrate separate, but these differ widely in appearance from the amorphous coagulum of albumin; are formed throughout the liquid after a short time; and are not produced with the diluted urine. Occasionally the urine contains resinous substances, usually administered as medicines, which with Heller's test give a zone resembling that produced by albumin. This may be distinguished by removing the portion of the liquid containing the ring by means of a pipette and shaking it in another test-tube with a little ether, when it will clear if it be resinous, but will remain cloudy if albuminous. Sometimes undiluted urines give no immediate reaction, and only a faint, ill-defined ring after standing, but the diluted urine gives an immediate and well-defined reaction; this is caused by the so-called nuclealbumin (p. 740). True mucin may also produce a faint opalescence, but no well-defined ring, and the opalescence disappears on slight rotation of the tube. The primary albumoses respond to the Heller test, but they redissolve on heating the test-tube, and they are not coagulated by heat, hence the heat test should always be used as well as the Heller.

(3) *Precipitation by Neutral Salts.*—Several tests are in use, based upon the precipitation of albumin from acid solutions by saturated solutions of neutral salts, such as ammonium sulfate, sodium sulfate, magnesium sulfate or sodium chlorid. *Roberts' reagent* consists of a saturated solution of sodium chlorid containing 5 per cent of strong hydrochloric acid, and filtered if necessary. The urine is floated upon the warmed reagent in the same manner as in the application of Heller's method; and a milky zone indicates the presence of albumin. Albumoses are also precipitated, but not urates; nor does the colored zone appear.

If acetic acid be added to albuminous urine to strongly acid reaction, and then an equal volume of saturated sodium sulfate solution, and the mixture boiled, the albumin is completely precipitated, while the albumoses remain in solution in the hot liquid. This reaction, designated as Panum's method, is utilized to free the urine from albumin in testing for albumoses (p. 739).

Other Precipitation Tests.—Several of the precipitation reactions of the albumins have been utilized for the detection of albumin in the urine. Prominent among these are the following:

(4) *Ferrocyanid Reaction.*—Acetic acid is added to the urine in such amount as to be present in the proportion of 2%, and then a 1:20 solution of potassium ferrocyanid drop by drop. A cloudiness or flaky precipitate is produced by serum albumin, serum globulin,

or primary albumoses, but the last named are redissolved by addition of much acetic acid and warming. The test is quite as delicate as the Heller. If the addition of acetic acid alone produce a cloudiness, it is due to the presence of mucin or of mucin-like substances, and the urine is to be filtered before addition of the ferrocyanid.

In the following tests the urine is to be floated upon the surface of the reagent in the same manner as in the application of the Heller test, and the characteristic appearance is also the formation of a milky zone.

(5) *Trichloroacetic Acid Reaction*.—This reaction is still more delicate than the Heller. A strong solution of the acid (sp. gr.=1.14) is used, or a crystal of the acid is dropped into the urine, and, dissolving, it forms a layer at the bottom. Serum albumin, serum globulin and primary albumoses respond to the test, but the last-named redissolve on heating, while the others remain. Excess of urates also gives rise to the same appearance as with the Heller reaction, and, similarly, its formation is prevented by previous dilution of the urine. The colored zone produced by urinary pigments in the Heller test is not formed with this or with the following reagents.

(6) *Spiegler's Reagent*—consists of 8 gms. of mercuric chlorid, 4 gms. of tartaric acid and 20 cc. of glycerol, dissolved in 200 cc. of water. A few drops of acetic acid are to be added to the urine for this test, which is said to be the most delicate of those for albumin. Its limit is placed at 1:250.000, and it is frequently observed with normal urine. The sp. gr. of urines below 1.005 is to be raised by addition of salt solution before application of the test. Primary albumoses give the reaction, but secondary albumoses (urinary peptone) do not.

(7) *Tanret's Reagent*—is made by dissolving 1.35 gm. of mercuric chlorid and 3.32 gms. of potassium iodid in separate portions of water, mixing the solutions, making the bulk up to 60 cc., and adding 20 cc. of glacial acetic acid. Secondary albumoses are also precipitated, but redissolve on heating. Certain alkaloids are also precipitated, but they are dissolved by ether shaken with the aqueous liquid, which then becomes clear. Several other reagents, containing mercuric salts (Bouchardat's, Jolle's, Zouchlos', Fürgringer's) are in use.

(8) *Oliver's Reagent* is one of several (Sonnenschein's, Maschke's, Jacwrowski's) containing tungstates or molybdates. It is a mixture of equal parts of a 20% solution of sodium tungstate, and 60% solution of citric acid. It precipitates secondary albumoses, which, however, dissolve on heating, and also alkaloids.

(9) *Roch's Reagent*, Salicylsulfonic acid, and (10) *Riegler's Reagent*, β -naphthol-o-sulfonic acid (asaprol), and orthophenol-sulfonic

acid (aseptol), are used in the same manner as trichloroacetic acid. They precipitate albumoses, which redissolve on heating.

(11) *Esbach's Reagent*—is one of several containing picric acid. It contains 10 gms. of picric acid and 20 gms. of citric acid in the liter. It is mixed with or floated upon the urine. It precipitates all proteins, also uric acid, creatinin and certain alkaloids.

(12) *Metaphosphoric Acid*—is best used in the form of *Blum's reagent*, which consists of a 10% solution of the acid, to which have been added 0.05 gm. of manganous chlorid, dissolved in a little dilute hydrochloric acid, and a little lead peroxid, and the solution filtered. The reagent should not be used if it have lost its pink color. It precipitates albumoses and uric acid.

The color reactions of the albumins (p. 577) cannot be conveniently used in testing for albumin in urine.

Test for Globulin.—Neutralize the urine exactly with ammonia, filter, and add an equal volume of neutral, saturated solution of ammonium sulfate: globulin separates as a white, flocculent precipitate. Albumin may be tested for in the filtrate from this precipitate by acidulation with acetic acid and heating. Excess of urates may give rise to a precipitate in using this test, but it is only formed after a time, is not flocculent, but granular, and is not white, but colored.

Quantitative Determination of Albumin and Globulin.—The only method of determining the quantity of "albumin" with any degree of accuracy is gravimetric. From 20 to 100 cc. of the clear urine (according as the qualitative testing has indicated a large or a small quantity of albumin) are made up to 100 cc. of liquid by addition of water, if necessary, and slowly heated. As the boiling temperature is approached, 2-4 drops of dilute acetic acid are added, and the mixture boiled for a few minutes, until the coagulated albumin has become flocculent, when it is collected upon a weighed filter, washed, first with water containing a little nitric acid, then with boiling water, then with alcohol, and finally once or twice with ether, dried at 110°, and weighed. For accurate determinations, the filter and coagulum are burnt and moderately ignited, the ash weighed, and its weight subtracted from that of the albumin found.

Quantitative Determination of Globulin.—One hundred cc. of the clear urine are accurately neutralized with ammonia, an equal volume of a neutral, saturated solution of ammonium sulfate is added and the mixture allowed to stand for an hour, after which the precipitated globulin is collected upon a weighed filter, washed with one-half saturated ammonium sulfate solution, dried at 110°, extracted with boiling water, then with alcohol, and then with ether, dried again at 110°, and weighed. The filter and contents are then burnt,

ignited, cooled and weighed, and the weight of the ash subtracted from the weight of globulin, plus ash, previously obtained. To determine the relation between albumin and globulin a determination of albumin and globulin, and another of globulin alone are made, as above directed: the difference is the amount of albumin.

Albumoses (Peptones).—Substances similar to the products of the action of digestive enzymes upon proteins occur in the urine pathologically. Peptones in the modern sense, i. e., not precipitable by saturation with ammonium sulfate, do not appear in the urine normally or pathologically. In the condition designated as "peptonuria," the so-called "urinary peptone" consists principally of substances closely resembling, if not identical with, the secondary albumoses, (deutero-albumoses, p. 615). Peptonuria in this sense occurs in diseases attended with the formation of large deposits of pus, in yellow atrophy and in abscess of the liver, in certain intestinal diseases, including typhoid, in tubercular ulceration, in scurvy, pyæmia, septicæmia, leucæmia, in diseases of pregnancy, in endocarditis, in pneumonia, in pleurisy, in diphtheria, in suppurative meningitis, and in certain forms of poisoning.

Primary albumoses, hetero-albumoses, have been met with in the urine (albumosuria) exceptionally in cases of osteomalachia.

The presence of albumoses is best detected by Panum's method (p. 736): acetic acid is added to strongly acid reaction and then an equal volume of saturated sodium sulfate solution, and the liquid is heated to boiling and filtered hot; albumoses are precipitated before the boiling, are redissolved on boiling, and are again precipitated from the filtrate on cooling.

If nitric acid be added to the hot filtrate from the coagulated albumin, produced by boiling a urine containing albumin and albumoses, no immediate precipitation occurs, but on cooling a white or yellow precipitate of albumose separates, which redissolves on heating, and reappears on cooling.

Heteroalbumose (primary albumose) gives the above reactions, and is further characterized by its action with the heat test: at a temperature of about 60° the urine becomes milky and deposits an imperfectly flocculent, gummy material, which adheres to the walls of the beaker, and which, in an acid liquid, dissolves on boiling, to reappear on cooling again.

For the detection of small quantities of secondary albumoses (urinary peptone) the method of Hofmeister, although intricate, is the most reliable. It consists in the complete removal of albumin by precipitation with ferric chlorid, the precipitation of the albumose with phosphotungstic acid, the decomposition of the precipitate, and the application of the biuret reaction to the solution of albumose.

The student is referred to more comprehensive treatises for the details of the process.

Mucin-like Substances.—The urine sometimes contains true mucins and nucleoproteids, produced in the urinary tract below the kidneys. The "nubecula" (p. 694) which separates as a delicate cloud from normal urine on standing, has for its chief protein constituent a substance resembling ovomucoid (p. 584), and designated as urinary mucoid. It is a glycoproteid, which on heating with dilute acids, yields a reducing substance, but no sulfuric acid (see below). It is soluble in dilute alkaline solutions, from which it is precipitated by acetic acid, but soluble in an excess of the acid. It is similarly precipitated by, and soluble in excess of mineral acids. It is not coagulated by heat, even in presence of sodium chlorid to saturation; but it is precipitated in the cold by saturation with magnesium or ammonium sulfate.

The substance usually referred to as nucleoalbumen, or as mucus, in the urine consists of different protein-coagulating substances, among which are nucleic acids, taurocholic acid, especially in *icterus*, and particularly

Chondroitin-sulfuric acid (p. 594), which is present in small amount in normal urine, and is increased in diseases involving the renal and vesical epithelium, as in acute and chronic nephritis and in cystitis, also in "functional" albuminuria, in *icterus*, and from the action of many poisons, notably of corrosive sublimate, arsenic, pyrogallie acid, naphthol and anilin. This substance exists in the urine, as well as in cartilage, in combination with albumins in the form of chondroproteids, or chondroalbumins.

The chondroproteids react with the Heller test, and their presence in excess is to be suspected when the urine becomes cloudy on addition of acetic acid in the cold, and gives a more distinct Heller reaction after dilution than when undiluted. To separate and identify chondroproteids a large volume of urine is treated with chloroform to prevent decomposition, and submitted to dialysis to remove salts; acetic acid is then added in the proportion of 2 p/m, and the mixture allowed to stand until the precipitate settles. This is then dissolved in the smallest quantity of dilute alkali and again precipitated with acetic acid. The precipitate is then heated on the water-bath with 5 per cent. hydrochloric acid and the solution divided into two parts, one of which is tested for its reducing action by Fehling's solution, and the other for sulfuric acid by barium chlorid.

A histon, a phosphorized protein, apparently identical with nucleohiston, has been met with in the urine in a case of leukæmia, and also in cases of peritonitis following appendicitis, pneumonia, erysipelas and scarlatina.

Hæmoglobin.—The blood coloring-matter may exist in the urine in the two conditions of hæmaturia and of hæmoglobinuria. The former is the consequence of a hæmorrhage somewhere in the urinary tract, the latter of profound alteration in the blood, and elimination of the liberated hæmoglobin. In the former condition the sediment contains blood-corpuscles, and sometimes blood-casts or small clots, and albumin is present in the urine, whose color is bright-red, reddish-brown, or dark-brown. The location of the hæmorrhage cannot be determined by examination of the urine, although it may be noticed that, if it is urethral, the last portions of the urine passed are free from blood; if it is renal, blood-casts are usually found in the sediment, and, if it is vesical, blood-clots of considerable size may be present.

Hæmoglobinuria, in which the urine contains oxyhæmoglobin or methæmoglobin in solution, with no blood-corpuscles, or very few, in the sediment, is most frequently the result of poisoning, as by hydrogen arsenid, potassium chlorate, pyrogallol and naphthol, but it also occurs in malarial fevers in the tropics, and after severe burns or after transfusion of blood. The urine varies in color from bright-red to dark-brown.

Tests for Blood-pigment.—(1) The urine, suitably diluted if necessary, gives the spectrum of oxyhæmoglobin, or that of methæmoglobin (p. 661). (2) *Heller's test*: the faintly acid urine is boiled, when a dirty brownish coagulum of albumin, containing the blood-pigment, is formed. Sodium hydroxid is added to the hot liquid, which then clears, becomes greenish in thin layers, and on standing deposits a red material having greenish reflections, which consists of phosphates and hæmatin. This precipitate may be collected and used for (3) *Teichmann's test* (p. 664). (4) *The guaiac reaction*: the urine is rendered faintly acid if not already so, and upon its surface is floated a mixture of equal parts of tincture of guaiac and old oil of turpentine. In the presence of blood coloring-matter a white zone is produced, which soon turns bluish, greenish, and finally a brilliant blue, and on gently shaking the tube the whole liquid is colored blue if the quantity of pigment is sufficient. In the reagent ozonic ether (ether containing hydrogen peroxid) may be used in place of oil of turpentine. Pus gives a similar color with tincture of guaiac alone.

Hæmatoporphyrin, related to urobilin and isomeric with bilirubin, is a normal constituent of the urine in small amount, but is notably increased in amount in poisoning by sulfonal, trional and tetronal, or even after long-continued medicinal administration of these remedies; also, in hepatic cirrhosis and in croupous pneumonia. Usually it colors the urine red, sometimes of a dark port-wine color,

but it may be present in considerable amount in urines which it colors only slightly. It is not accompanied by albumin.

To test the urine for hæmatoporphyrin 100 to 200 cc. are precipitated with 10% sodium hydroxid solution; the precipitate, of phosphates and coloring-matter, is dissolved in about 10 cc. of alcohol acidulated with hydrochloric acid, and the solution is examined with the spectroscope (p. 665). If the result be negative the alcoholic solution is rendered alkaline with ammonium hydroxid, the precipitate dissolved in a little dilute acetic acid, agitated with chloroform, and the chloroform solution again examined spectroscopically.

Biliary Constituents.—The urine may contain the biliary salts and pigments as a consequence of reabsorption of bile, caused by obstruction of the biliary ducts, or when the blood-pressure in the liver is lowered (hepatogenic icterus); or the biliary pigments may appear in the urine in consequence of their formation in the system elsewhere than in the liver, as hæmatoidin is produced from the blood coloring-matter (p. 640), as in pernicious anæmia, malaria, typhoid, and in poisoning by hydrogen arsenid (hæmatogenic icterus). Urine containing bile is golden-yellow or greenish-brown in color, and the epithelium which it contains is also dyed yellow. It is usually cloudy, contains albumin, and, when shaken, forms a yellow, persistent froth upon its surface.

The biliary salts are rarely tested for, because the examination for the equally characteristic coloring-matters is much more easily conducted. They may, however, be detected by the Pettenkofer reaction, if care be had to avoid possible sources of error from other substances which also respond to the test. To this end the urine is concentrated, extracted with alcohol, and the alcoholic extract filtered and freed from alcohol by evaporation. The residue is dissolved in a little water and precipitated with lead acetate and ammonia. The lead precipitate is collected, washed, extracted with boiling alcohol, which is filtered off hot, treated with a little sodium hydroxid solution and evaporated to dryness. The residue is extracted with a little absolute alcohol, the solution mixed with about ten volumes of perfectly anhydrous ether, the precipitate collected on a small filter, washed with a little ether, dissolved in a small quantity of water and tested by the Pettenkofer method as directed on p. 636.

For the detection of the biliary coloring-matters the reactions described on p. 637 are used. The Gmelin reaction may be modified to Rosenbach's method, which consists in filtering the urine through a small filter, and touching the dried filter with a drop of nitroso-nitric acid, when the colors are produced in rings about the drop. This reaction is not satisfactory in dark urines containing excess of indican. In using Hammarsten's reaction with urines containing

blood coloring-matter, or very small quantities of bile pigments, a preparatory treatment is required, which consists in adding barium chlorid to the urine, centrifugating, pouring off the supernatant liquid, shaking the sediment with 2 cc. of the reagent, and centrifugating again, when a bluish-green solution is obtained. Smith's reaction may also be used: float dilute tincture of iodine (1:10) on the urine, when the biliary pigments form a green ring at the union of the two layers.

Other Abnormal Pigments—*Urorosein* is a coloring-matter, not present in normal urine, but appearing in a variety of abnormal conditions, as in diabetes mellitus, chlorosis, osteomalachia, nephritis, typhoid fever, phthisis, pernicious anæmia, etc. It exists in the urine as a chromogen, from which it is formed by the action of acids, and, when so liberated, communicates a rose-color to the urine. It produces the rose-colored ring so frequently observed in applying the Heller test to the pathological urines. To demonstrate its presence 10 cc. of 1:4 sulfuric acid are added to 50 cc. of urine, which are then shaken with a few cc. of amyl alcohol, and the amyl alcohol examined spectroscopically. Urorosein gives a spectrum of one band between D and E, and in concentrated solution, allows only the red and orange rays to pass. The color is discharged by alkalis, and returns on addition of acids, it is also discharged by agitation of its acid solution with powdered zinc, and reappears soon by exposure to air.

Melanin is formed from melanogen on exposure to air of the urine of patients with melanotic tumors. Such urines are normal in color when first voided, but become dark or even black on standing. They may be distinguished from urines behaving similarly from the presence of derivatives of carboic acid, salol, etc., by the facts that they give with bromine-water precipitates which, although at first yellow, gradually change to black, and that with ferric chlorid they give precipitates which are at first gray, changing to black.

Alkaptonuria is another rare condition in which the urine, normally colored at first, turns dark on standing, and which occurs in individuals suffering from tuberculosis or from cerebral tumors. It is due to the presence of aromatic oxyacids, notably of **glycosuric acid** (pp. 460, 461) which on decomposition yield colored phenolic derivatives, probably similar to those which color the urine in poisoning by phenols and diphenols. Glycosuric acid is also of interest in connection with the testing of urine for sugar in dark-colored urines, because it reduces the cupric salts (Fehling's test, etc.), although it does not reduce those of bismuth (Boettger's test), and it does not ferment.

Ehrlich's Diazo-reaction.—The urine in typhoid fever contains a

substance which gives a more or less intense red color with diazo-benzene-sulfonic acid and ammonia. The reaction, which can be obtained with typhoid urine usually on the fifth or sixth day, but not later than the twenty-second, was at first said to be pathognomonic of that disease, but it is also obtained with the urine of acute pulmonary phthisis, in which, however, it does not appear before the third week and continues to the end, and also in scarlatina, measles, smallpox and other acute febrile diseases. The reagent used is most conveniently kept in two solutions: (1) a saturated solution of sulfanilic acid in a mixture of 50 cc. of hydrochloric acid and 950 cc. of water; and (2) a 0.5 per cent. solution of sodium nitrite. When used 1 cc. of (2) is added to 40 cc. of (1) and the mixture shaken. Equal volumes of the urine and the reagent are shaken together in a test-tube and 1-2 cc. of ammonia are floated upon the surface of the mixture, when, in an affirmative result, a red band is formed at the junction of the liquids. Or a better method of applying the test consists of adding 50 cc. of absolute alcohol to 10 cc. of urine, filtering, adding 20 cc. of the reagent gradually from a burette to 30 cc. of the filtrate in an Erlenmeyer flask, with agitation after each addition, and then slowly adding ammonia, when a red color is produced, which remains permanent when the ammonia has been added in excess. Urines containing biliary pigments become very dark and cloudy.

To what substance in the urine this reaction is due is still unknown. The reaction is, however, given intensely by histidin and by tyrosin, and by sturin, edestin and other proteins from which histidin or tyrosin is obtainable, but not by other protein split products.

Glucose.—Affirmative results, not only with the copper reduction tests, which might be due to uric acid, creatinin, or glucuronates, but also with the phenylhydrazin and benzoyl chlorid reactions, which are not open to this objection, have demonstrated that perfectly normal urine contains glucose. But the sugar is normally present in such small amount that it does not respond to the sugar tests as usually applied. When it does respond to these it is present in abnormal amount, and the symptom known as **glycosuria** exists. This may or may not be due to a pathological condition.

Normally the glucose content of the blood varies within narrow limits, 0.5 to 1 p/m, and in this quantity the kidneys present a barrier to its passage into the urine, except in the minute amounts above referred to. In the condition known as **phloridzin diabetes**, in which glycosuria follows upon the administration of phloridzin, it is believed that the phloretin component of the glucosid exerts a toxic action upon the kidney cells by which their retaining power is diminished or

abolished. All other non-toxic glycosurias are the consequence of **hyperglykæmia**, i. e., an excess of glucose in the blood. This may be due either to over-production of glucose, or to impediment to its oxidation to CO_2 and H_2O , which is its normal final destiny. Clearly, therefore, the consideration of glycosuria in some of its aspects is inseparable from that of the glycogenic function of the liver, and what we are about to say must be considered as being in amplification of what has already been said concerning the action of the liver upon carbohydrates (pp. 681, 683), apology being offered for some unavoidable repetition.

One of the earliest observations with regard to glycosuria was the classic one of Cl. Bernard, that a lesion of a certain area in the floor of the fourth ventricle in the medulla is followed in one to two hours by glycosuria, which persists for five to six hours in rabbits, and as long as seven days in dogs. It has since been shown that this glycosuria is due to hyperglykæmia, consequent upon excessive conversion of glycogen into glucose in the liver, resulting from a disturbance of the nerve supply of that organ in a manner with which we are not concerned here, beyond the fact that the normal governing influence of the "center of sugar regulation" in the medulla is transmitted through the pneumogastric and the splanchnic nerves. First it was found that the operation was successful with well-nourished animals, i. e., those which had a glycogen reserve; but failed entirely with starved, glycogen-poor animals; and also that in animals killed some little time after the puncture the liver was found to be glycogen-free. That these phenomena are due to loss of power of the liver to store glycogen is shown by the fact that if, in an animal made as glycogen-free as possible by starvation, a solution of glucose be injected into the mesenteric vein, only a little sugar appears in the urine; but if the same experiment be made with an animal upon which the puncture has been made, a copious glycosuria soon follows. That the liver is the only organ affected by the puncture is shown by the fact that glycosuria does not follow after ligation of the hepatic vessels. There has been much speculation with regard to the mechanism of puncture-glycosuria, but nothing definite has been established. The supposition is, however, plausible that under normal conditions glycogen is contained in the liver cells, not merely deposited in its own form, but in a condition of more or less loose combination, in which it is protected from the action of the hepatic diastase, and that the result of the disturbance of regulation is to suddenly liberate the glycogen from this compound, and expose it to the action of the enzyme. Glycosuria is also produced by a method involving no mechanical injury to the center in the medulla, but exerting upon it a toxic action. This is also, by the way, in support of the view now entertained that the calcium

salts are more "normal" to the system than are those of sodium. The intravenous injection of a 1 per cent sodium chlorid solution is followed by glycosuria, and the same effect is produced by solutions of other sodium salts, NaI, NaBr and NaNO₃. This glycosuria is not produced if the splanchnic nerves have been previously divided, and it is arrested by intravenous injection of calcium chlorid solution, but may be again provoked by further injection of sodium salt, and in a degree proportionate to the concentration of the solution. That the action of the sodium salt is upon the center in the medulla is rendered highly probable by the fact that, if the axillary artery be ligated, injection of the salt solution into the artery on the central side of the ligature is followed by much more prompt and intense glycosuria than is injection into the vessel on the peripheral side of the ligature.

The condition known as pancreatic diabetes is an instance of a glycosuria dependent upon deficient consumption of sugar, which may or may not be associated with normal production, as in any event, if the balance be disturbed in that direction, there will be accumulation and hyperglykæmia, and, in fact, in the operative pancreatic glycosuria, referred to below, the sugar content of the blood is above the normal. If the pancreas be totally extirpated in dogs, an intense glycosuria results. The extirpation of the gland must be complete to insure the occurrence of glycosuria, as frequently it does not result if a minute fraction be allowed to remain, whether in communication with the duct or not, or even if a small fragment be transplanted under the skin, and the remainder of the gland completely removed. But removal of this remaining fraction is followed by glycosuria. With partial extirpation of the gland, however, glycosuria sometimes follows and sometimes does not, from which it may be inferred that all parts of the gland are not equivalent in their action in this regard. That the glycosuria does not depend upon interference with digestion of the carbohydrates by the pancreatic secretion is shown by the facts that it does not follow after ligation of the duct, or even after removal of that portion of the pancreas which is in more direct communication with the duct, so long as a small fraction of the gland tissue is allowed to remain. It might be supposed that the pancreas may act, something after the manner of the liver, by holding back substances whose presence in the blood would prevent the normal carbohydrate metabolism. Were this the case, transfusion of blood from a depancreatized animal to a normal one would cause glycosuria in the latter. But that this does not occur has been demonstrated. The pancreas therefore exerts its governing action in carbohydrate metabolism upon some other glucose-producing or glucose-consuming organ. That the glycosuria does not depend upon the suppression of an influence of the pancreas which favors the glycogen-forming power of the liver,

and the consequent flooding of the system with glucose from the intestine, is shown by the facts that after the death of depancreatized animals, the liver is found not to have suffered the loss of weight which all other organs have sustained, and to be rich in glycogen. The chief seat of glucose consumption in the system is in the muscles. That pancreas glycosuria depends upon an interference with this destruction is shown directly by the fact that a fluid obtained by great pressure from muscular tissue does not decompose glucose, nor does a liquid similarly obtained from the pancreas, but a mixture of the two liquids destroys sugar energetically. It may be inferred that the pancreas produces an internal secretion which activates the sugar-destroying function of the muscle, as the formation and activity of trypsin depend upon secretin and enterokinase. Whether this secretion is or is not the product of the cells of the Langerhans islands of the pancreas is not determined, although it would seem that it might be, as these cells have been found to exert a decomposing action upon glucose.

Normally, glucose is oxidized in the system to carbon dioxide and water. But there must be a limit to the amount of carbohydrate food which can be utilized by the economy in a given time. This limit seems to vary in different individuals, but may be placed at an amount of total carbohydrate equivalent to 100 to 200 gms. of glucose in twenty-four hours, and probably when glycosuria exists with a daily ingestion of 100 gms., or less, of glucose equivalent it is due to a pathological condition. It is not immaterial in what form the carbohydrate is taken. If taken principally as glucose, which under ordinary conditions of life is most unusual, absorption will be rapid and the blood will shortly become surcharged with glucose, and a temporary glycosuria will result with relatively small quantities.

Non-pathological glycosuria may be observed: (1) with a diet containing more than 200 gms. of glucose-equivalent in twenty-four hours. A pathological alimentary glycosuria occurs with less than 100 gms. glucose-equivalent, in hepatic and pancreatic disease and in certain cerebral diseases; (2) in pregnancy and during lactation there is apparently a diminution in the power to utilize carbohydrate material, and glycosuria frequently exists with a diet containing less than 100 gms. of glucose-equivalent in 24 hours, the daily elimination sometimes rising as high as 30 gms., but being more usually less than 3 gms. It appears towards the end of gestation, and does not disappear entirely until the suppression of the lacteal secretion; (3) in nursing children from about the eighth day to ten weeks; (4) in old persons (70 to 80 years); (5) in extremely stout persons, particularly in females at the menopause, the elimination sometimes reaching 8 to 12 gms. in 24 hours.

Pathological glycosurias may be divided into "transitory," in which the quantity of sugar is not large, and its presence not constant; and "permanent," in which sugar is constantly present and frequently in very large amount. *Transitory glycosuria* occurs in certain hepatic derangements, congestion, cirrhosis and amyloid degeneration; in many diseases of the central nervous system, with tumors or hæmorrhages at the base of the brain, in meningitis, concussion, fracture of cervical vertebræ, railway injuries, in epileptic and apoplectic seizures, and also in certain diseases of the peripheral nervous system, as in sciatica and in tetanus; in acute febrile diseases, pneumonia, typhoid, acute articular rheumatism, scarlatina, etc., particularly during convalescence, when the elimination may reach 5 to 50 gms. in 24 hours; under the influence of many poisons, such as curare, chloral, carbon monoxid, morphin, arsenic, and the anæsthetics.

Persistent pathological glycosuria is observed principally in two conditions: (1) In lesions of the brain involving the floor of the fourth ventricle; (2) in diabetes mellitus. In this latter condition the sugar may temporarily disappear from the urine, particularly in the earlier stages of the disease, in the early morning urine, and upon regulation of the diet by exclusion of carbohydrates. There is a diurnal variation in the elimination of sugar, the amount passed being less during the night than during the day, the maximum being reached about four hours after the principal meal, and the minimum six or seven hours thereafter. There is great polyuria, the quantity of urine in 24 hours reaching as high as 50 liters. The quantity of sugar varies greatly; an elimination of 200 gms. in 24 hours is by no means uncommon, but, even with this large amount, the elimination may cease entirely, particularly in the morning urine, by exclusion of carbohydrates from the diet, under the influence of intercurrent diseases, or in the later stages, upon the appearance of diabetic coma. Instances have occasionally been reported in which the elimination has reached 400 to 600 gms. in 24 hours, and one instance in which 1376 gms. were discharged in one day. In other severe cases, terminating fatally, the quantity of sugar eliminated has not been large at any time, not exceeding 10 gms. in 24 hours. The non-disappearance of the sugar from the urine on exclusion of carbohydrates from the diet is usually considered as indicating a more serious condition, even if the quantity be small, than the elimination of a large amount which ceases under those circumstances. The specific gravity of diabetic urine is usually high, 1030 to 1060, but it may be as low as 1012. In true diabetes there is not only glycosuria, but also azoturia, and the increase in the elimination of nitrogen appears to offer a better measure of the intensity of the

disturbance than variations in the amount of sugar. In the later stages acetone, fatty acids and fats also appear in the urine (see below).

As has been already indicated (p. 745), glycosurias other than those due to nervous lesions may have their origin in an inability of the liver to transform the carbohydrates into glycogen, or to inability of the muscles to utilize the carbohydrate material, or to diseases of the pancreas.

Examination of Urine for Glucose.—The following procedure is recommended for qualitative examination of urine for glucose: If the urine be albuminous, it is indispensable that the albumin be separated before any of the tests for sugar are applied. This is done by heating the urine gradually to boiling, with addition of very dilute acetic acid as the boiling temperature is approached, heating until the coagulated albumin has separated in flocks, and filtering.

Nylander's modification of the Böttger test (p. 325) is then applied to the albumin-free urine. This test is preferable to the copper reduction tests, as it does not react with uric acid, creatinin or the glycosurates (p. 743), which may reduce the copper reagents. But it is open to the objection that with urines voided after chloroform narcosis and with those containing mercury, whether from the medicinal administration of mercurials to the patient or from addition of HgCl_2 to the urine as an antiseptic, the reaction, even in the presence of glucose, does not give the characteristic black color, but at most a yellow or brown. Therefore, if the Nylander reaction give a negative result, the Fehling test (p. 324) is to be resorted to. An affirmative result with the Nylander indicates the presence of glucose, or of conjugate glucuronates, other ketoses or aldoses, or other reducing agents. Negative results with both Nylander and Fehling indicate the absence of sugar. If either reaction give an affirmative result, a further examination by another test is still required.

A Smith's fermentation tube is then filled with the urine to which yeast has been added, and placed in an incubator, heated to about 37° , for twenty-four hours. The efficiency of the yeast must be assured by blank testing with water and glucose solution (p. 327). If fermentation do not occur, glucose is absent. If it do occur the presence of glucose or of some other fermentable sugar, fructose or maltose, is indicated. If the Nylander test, applied to the urine after complete fermentation, give an affirmative result, the presence of a reducing substance, other than a sugar, and accompanying such sugar, is indicated.

The presence of fructose is indicated by an affirmative reaction with Seliwanoff's test (p. 326), and by either a laevorotation with the polariscope or a lower quantitative result with the polariscope than

with Knapp's or Fehling's methods (below). If the urine ferment, and is dextrorotary, and if the quantitative result obtained by the polarimeter be less than that obtained by the reduction methods, both glucose and fructose are present. Maltose very rarely occurs in urine, and when it does it is accompanied by glucose. It is said that glucose and maltose may be distinguished from each other by the difference in the fusing points of their osazones, but as these fusing points approach each other closely: 204° to 205° and 206° , this method of distinction cannot be reliable. The phenylhydrazin test (p. 325) may, however, be applied in confirmation of the Nylander and fermentation tests. It does not react with reducing agents other than sugars, nor with uric acid, creatinin or conjugate glucuronates, although it does with free glucuronic acid, which is, however, never present in urine.

Quantitative Determination of Glucose.—(1) *By the Polarimeter.*—Preparatory to polariscopic examination the liquid must be rendered transparent and colorless, or nearly so. This is accomplished in the case of the urine and other organic liquids by isolation of the sugar, by precipitation either by basic lead acetate, or by benzoyl chlorid, liberation of the sugar and resolution in water. Either operation is rather intricate, and the student is referred to more comprehensive treatises for their description. The clear, decolorized urine is observed by the polarimeter (p. 37), and the mean of half a dozen readings taken as the angle of deviation. From this the percentage of sugar is determined by the formula $p = \frac{a}{52.6 \times l}$, in which p = the weight, in grams, of glucose in 1 cc. of urine; a = the angle of deviation; l = the length of the tube in decimeters. The same formula may be used for other substances by substituting for 52.6 the value of $[a]_D$ for that substance. Or a saccharimeter, which is a polarimeter graduated to read the percentage of glucose directly, may be used. If the urine contain albumin, it must be removed before determining the value of a .

The results of this method must always be controlled by those of other methods, as the dextrorotation of glucose may be diminished or overcome by the laevorotation of fructose, conjugate glucuronates, or β -oxybutyric acid. The determination is, however, often of value for identification and determination of these substances.

(2) *Knapp's Method.*—This method, based upon the reduction of mercuric cyanid by glucose, is preferable to the more commonly used Fehling, because the end reaction is sharper, and daylight is not necessary, as it is with the Fehling.

If the qualitative testing have shown the presence of a reducing substance other than glucose (p. 749), this must be removed by Focke's

method (p. 324) before proceeding with either Knapp's or Fehling's quantitative process.

The standard solution consists of 10 gms. of pure, crystallized mercuric cyanid and 100 cc. of a solution of sodium hydroxid, sp. gr. 1.145 in a liter. Twenty cc. of this solution are reduced by 0.05 gm. of glucose. The solution is used in the same way as Fehling's solution: 20 cc. of the solution are diluted with 80 cc. of water and heated in a flask to boiling. The urine, diluted with water in the proportion of 1:4 or of 1:9, is added from a burette, at first in portions of 2 cc., then of 1 cc., then of 0.5 cc. and finally of 0.1 cc. As the end reaction is approached, the liquid clears, and the mercury deposits. A drop of liquid is then removed from time to time with a capillary tube, placed upon a piece of filter paper, and held, first over a bottle containing strong hydrochloric acid, then over one containing a strong solution of hydrogen sulfid, until it no longer assumes a yellow or brown color. The calculation is the same as with Fehling's solution, and the result is multiplied by two. The end reaction

(3) *By Fehling's solution.*—The copper contained in 20 cc. of Fehling's solution (p. 324) is precipitated by 0.1 gm. of glucose.

To use the solution, 20 cc. of the mixed solutions are placed in a flask of 250–300 cc. capacity, 80 cc. of distilled water are added, the whole thoroughly mixed and heated to boiling. On the other hand, the urine to be tested is diluted with four times its volume of water if poor in sugar, and with nine times its volume if highly saccharine (the degree of dilution required is, with a little practice, determined by the appearance of the deposit obtained in the qualitative testing); the water and urine are thoroughly mixed and a burette filled with the mixture. A little CaCl_2 solution is added to the Fehling's solution and the diluted urine added, in small portions toward the end, until the blue color is entirely discharged—the contents of the flask being made to boil briskly between additions from the burette. When the liquid in the flask shows no blue color when looked through with a white background in daylight the reading of the burette is taken. This reading, divided by five if the urine was diluted with four volumes of water, or by ten if with nine volumes, gives the number of cc. of urine containing 0.1 gram of glucose; and consequently the elimination of glucose in 24 hours, in decigrams, is obtained by dividing the number of cc. of urine in 24 hours by the above result.

Example.—20 cc. Fehling's solution used, and urine diluted with four volumes of water.

Reading of burette: $36.5 \text{ cc.} \times \frac{36.5}{5} = 7.3 \text{ cc.}$ urine contain 0.1 gram glucose. Patient is passing 2,436 cc. urine in 24 hours. $\frac{2,436}{7.3} = 333.6$ decigr. = 33.36 grams glucose in 24 hours.

(4) *Gravimetric method.*—When more accurate results than are obtainable by Fehling's volumetric process are desired, recourse must be had to a determination of the weight of cuprous oxid obtained by reduction. A small quantity of freshly prepared Fehling's solution, diluted with four times its volume of boiled water, is heated to boiling in a small flask. To it is gradually added, with the precautions observed in the volumetric method, a known volume of the diluted urine, such that at the end of the reduction there shall remain an excess of unreduced copper salt. The alkaline fluid is separated as rapidly as possible from the precipitated oxid, by decantation and filtration through a small double filter, and the precipitate and flask repeatedly washed with hot H_2O until the washings are no longer alkaline. A small portion of the precipitate remains adhering to the walls of the flask. The filter and its contents are dried and burned in a weighed porcelain crucible. When this has cooled, the flask is rinsed out with a small quantity of HNO_3 ; which is added to the contents of the crucible, evaporated over the water-bath, the crucible slowly heated to redness, cooled, and weighed. The difference between this last weight and that of the crucible + that of the filter-ash, is the weight of cupric oxid, of which 220 parts = 100 parts of glucose. Or better, the cupric oxid is dissolved in a little dilute nitric acid, the solution evaporated with a little sulfuric acid, the residue redissolved, and the copper determined electrolytically: 175.6 Cu. = 100 glucose.

(5) *By specific gravity; Robert's method.*—The sp. gr. of the urine is carefully determined at 25° (77° F.); yeast is then added, and the mixture kept at 25° (77° F.) until fermentation is complete; the sp. gr. is again observed, and will be found to be lower than before. Each degree of diminution represents 0.2196 gram of sugar in 100 cc. of urine.

Other Sugars—*Lævulose* (fructose)—sometimes occurs in diabetic urine. When it is present the urine responds to the tests for glucose, but it either rotates to the left or has a dextrogyratory action less than that required by the result of the quantitative reduction methods.

Lactose occurs in the urine after the ingestion of large quantities of milk-sugar, and sometimes in the urine of women during the later stages of gestation and during lactation. Its presence may be inferred when the urine reacts with the copper and bismuth tests, but gives negative results with the fermentation test.

Maltose rarely accompanies glucose in pancreatic diabetes.

Laiose is a substance which occurs in the urine in some cases of diabetes. It is lævogyrous and amorphous, it reduces the compounds of copper and of bismuth, does not ferment, and forms a

yellow or brown oily material with phenylhydrazin. It is supposed to be a sugar.

Pentoses (p. 310) have been met with in large amount in the urine of persons addicted to the morphin habit, in whom there is an alternation of glycosuria and pentosuria. The pentoses are detected by Tollens' reaction: the urine is mixed with an equal volume of strong hydrochloric acid, a little phloroglucin is added, and the liquid heated by immersion in a boiling water-bath. A red-violet color indicates the presence of pentoses, galactose, lactose, or glucuronic acid. To distinguish between these the liquid is examined with the spectroscope, when, in the presence of pentoses or of glucuronic acid, a band is seen in the green, between D and E. The pentoses and glucuronic acid may be distinguished by the fusing points of their osazones, that of glucuronic acid fusing at 115° , and those of the pentoses at a higher temperature, 160° .

Inosite, muscle sugar, is a cyclic alcohol, $C_6H_6(OH)_6$, which occurs in traces in normal urine, and in increased amount in albuminuria, in diabetes insipidus, and after ingestion of large quantities of water.

Acetone Bodies.—Three substances are included under this head, which are evidently successive products of the same process. They are β -oxybutyric acid, $CH_3.CHOH.CH_2.COOH$, acetylacetic acid, $CH_2.CO.CH_2.COOH$, and acetone, $CH_3.CO.CH_3$. Clearly acetylacetic acid is a product of oxidation of β -oxybutyric acid, and this in turn yields acetone by loss of CO_2 . The oxybutyric acid is the *laevo* acid. Of these substances acetone is constantly present in normal urine, the daily elimination being from 0.001 to 0.01 gm.; acetylacetic acid may be present without β -oxybutyric acid, but never without acetone, and β -oxybutyric acid never occurs in normal urine. Probably the occurrence of these substances in these relations indicates varying degrees of interference with a normal process of oxidation through them. When acetone bodies are present in the urine in quantities greater than the normal traces the symptom is known as **acetonuria**. When acetonuria exists acetone is also eliminated by the lungs, and, when present in sufficient amount, communicates a peculiar, sweet, apple-like odor to the breath. The condition of acetonuria is accompanied, except in the rabbit, by a notable increase in the percentage elimination of ammonia, which may rise as high as 35 to 40 per cent of the total nitrogen. Acetonuria occurs in normal individuals, particularly stout persons, with deprivation of food, in febrile diseases when the febrile condition is prolonged, in certain mental diseases, such as general paresis, melancholia and epilepsy, after chloroform narcosis, in puerperal eclampsia, and in diabetes.

In considering the origin of these substances, the probability of

their being derived from the carbohydrates would first suggest itself, but pronounced acetonuria frequently occurs in diabetics from whose diet carbohydrates are excluded, and in these patients, as well as in other forms of acetonuria, the condition may be diminished in intensity, or even entirely removed, by adding carbohydrates to the diet; and acetonuria is developed in diabetics by complete exclusion of carbohydrates from the food.

The increased elimination of ammonia in acetonuria indicates a disturbance in the protein metabolism, probably a failure on the part of the liver to convert ammonia into urea. But the appearance of the acetone bodies in the urine is not an indication of increased protein decomposition, as the total nitrogen is not increased during fasting, but is diminished, while that of the acetone bodies is increased. It has also been observed that a diabetic may remain in nitrogenous equilibrium, or may even gain nitrogen, without the degree of acetonuria being affected. In one observed case, a diabetic with a protein consumption of 262 gms. in three days, eliminated 342 gms. of β -oxybutyric acid.

But, while the manner and degree in which the proteins are concerned in acetonuria are undetermined, there is positive evidence that the condition depends to a great degree upon fat consumption, and that it occurs in conditions in which the organism is burning its own fat deposits. This is certainly true in inanition under ordinary conditions, and it has been shown that the increased elimination of acetone bodies by women in the puerperal state is pronounced in fat women, but not in those having little fat reserve. While addition of proteins or of carbohydrates to the diet in acetonuria may diminish the amounts of acetone bodies eliminated, the contrary result follows the addition of fats.

The occurrence of acetone bodies, and notably of acetylacetic and β -oxybutyric acids in the blood in diabetes and other conditions attended with acetonæmia was supposed to produce acidism or acidosis, by which the normal and necessary alkalinity of the blood was diminished. Usually, however, this does not occur, as the ammonia also produced neutralizes the acids, and prevents their action upon the blood alkalies. This is shown to be the case by the fact that rabbits, in which the attendant formation of ammonia does not occur, are exceedingly susceptible to the form of poisoning referred to as acidism, and in them the symptoms of increasing dyspnoea, subnormal temperature, somnolence, coma, and convulsions may be developed by merely withholding food capable of producing alkalies. There may also occur a sudden and sufficiently excessive formation of these substances in diabetics as the similarly operating cause of the like symptoms which occur in diabetic coma.

Tests for the Acetone Bodies.—As acetylacetic acid is decomposed, with formation of acetone, by simple heating of the urine, this must first be tested for, and removed, if present, before examining for acetone.

Acetylacetic Acid.—(1) *Arnold's Test:* The reagent is in two solutions: One a 1 per cent solution of sodium nitrite, the other a solution made by dissolving 1 gm. of para-amidoacetophenone in 100 cc. of water, and adding HCl until the yellow liquid becomes colorless. One volume of the first solution is mixed with two of the second to produce the reagent. Equal volumes of the reagent and the urine are shaken together and a few drops of ammonia are added, when an amorphous reddish-brown precipitate is produced, which develops a purple-violet color when the mixture is treated with 10 to 12 volumes of concentrated HCl.

(2) *Gerhardt's Test:* Add dilute solution of neutral ferric chlorid so long as a precipitate (of phosphates) is formed, filter, and add more ferric chlorid solution, a wine-red color is produced if acetylacetic acid be present. If the result be affirmative it should be confirmed by: (1) Render a portion of the urine faintly acid, boil, cool, and repeat the test, which should give a negative result; (2) acidulate another portion with dilute sulfuric acid, agitate with ether, and then agitate the separated ether with dilute ferric chlorid solution, which should be colored wine-red.

Acetone.—If there be no acetylacetic acid present the urine is tested for acetone as directed below, but if it be present the urine is rendered faintly alkaline, agitated in a separator with a mixture of alcohol and ether, the ether separated, agitated with water, and the water tested for acetone by the tests given below. In the absence of acetylacetic acid a liter of the urine is acidulated by addition of 1 gm. of phosphoric acid, and distilled; 30 cc. of distillate being collected and tested by:

(1) *Lieben's Iodoform Test.*—Add caustic soda and a little solution of iodine in potassium iodid, and warm: the odor of iodoform is produced, and a yellow, crystalline precipitate, if the quantity be sufficient. Also reacts with alcohol. Or Gunning's modification of this test, which has the advantage of not reacting with alcohol or aldehyde, may be used: An alcoholic solution of iodine and ammonia are used in place of the aqueous iodine solution, which causes the formation from acetone of iodoform and the black nitrogen iodid, which latter gradually disappears on standing, leaving the iodoform.

(2) *Legal's Nitroprussid Test.*—Add a few drops of a freshly prepared solution of sodium nitroprussid, and then KHO or NaHO solution, when, in presence of acetone, the liquid is colored ruby-red, and, on supersaturation with acetic acid, changes to purple.

Paracresol gives a yellow-red color, which changes to yellow with excess of acetic acid. Creatinin gives an initial color with this test similar to that produced by acetone, but on addition of acetic acid, it turns to yellow, and slowly to green or blue. But creatinin cannot be the source of error if the urine has been distilled as above directed.

(3) *Reynold's Mercuric Oxid Test*—is based upon the property of acetone to dissolve freshly precipitated mercuric oxid. Mercuric oxid is precipitated from a solution of mercuric chlorid by addition of an alcoholic solution of potassium hydroxid, and a portion of the distillate is added to the mixture, which is then strongly shaken and filtered. The formation of a black precipitate by addition of ammonium sulfid to the filtrate indicates that it contains dissolved mercuric oxid.

(4) *Penzold's Indigo Test*.—Add a portion of the distillate, and then NaHO solution to solution of orthonitrobenzaldehyde, prepared by making a hot saturated solution and cooling it, when, in presence of acetone, the liquid turns yellow, then green, and finally deposits indigo-blue. If chloroform be then shaken with the mixture it forms a blue solution at the bottom of the test-tube.

The principle of Lieben's reaction is utilized in the Messinger-Huppert method of quantitative determination of acetone, the amount being calculated from the quantity of iodine used in the formation of iodoform.

β -oxybutyric Acid.—An examination for this acid is not called for except acetylacetic acid have been found to be present. In that event, if the urine be laevorotary after complete fermentation, the presence of β -oxybutyric acid is probable. *Kulz's Method*, based upon the dehydration of this acid to crotonic acid: $\text{CH}_3.\text{CHOH}.\text{CH}_2.\text{COOH} = \text{CH}_3.\text{CH}:\text{CH}.\text{COOH} + \text{H}_2\text{O}$ is then to be used: The fermented urine is evaporated to a syrup, an equal volume of concentrated H_2SO_4 is added, and the mixture distilled. The distillate on cooling deposits crystals which, after drying, fuse at $71-72^\circ$. If no crystals are deposited the distillate is extracted by agitation with ether, the ethereal solution evaporated, and the f. p. of the residue determined.

Amido Acids.—The question whether amido acids may normally be present in the urine has been much discussed. Until quite recently the only member of the class which has certainly been extracted from normal urine was glycocoll. But, as the process of its extraction involved long heating with alkaline solutions, it may be questioned whether the amido acid did not result from decomposition of hippuric acid. It is quite within the possibilities, however, that, as a synthesis of hippuric acid from glycocoll and a benzoyl derivative takes place in the kidneys, one constituent might under normal conditions be present

in sufficient excess to be eliminated. Recently a substance has been obtained from normal urine by the β -naphthalenesulfochlorid method which had the crystalline form of leucin and produced a copper compound having the characters of that of leucin. The question must be considered as still open.

The two pathological conditions in which amido acids occur in the urine are yellow atrophy of the liver and acute phosphorus poisoning, in both of which there is extensive disorganization of liver tissue. The two amido acids which first attracted attention in this connection were leucin and tyrosin, which have also been said, upon evidence which must be considered as insufficient, to occur in the urine in other pathological conditions, as in typhoid and in variola. The presence of leucin and tyrosin has usually been predicated upon the occurrence of certain crystals or nodules in the urinary deposits. It has been shown, however, that, while these may in some instances consist of leucin or tyrosin, they do not always, and therefore their occurrence is insufficient evidence of the presence of these substances.

The presence of tyrosin, and of tyrosin, leucin and glycocoll, in the urine in acute phosphorus poisoning has been demonstrated by more modern methods in several instances, and in a recent case tyrosin, leucin, alanin, glycocoll and arginin were found and identified: tyrosin by its crystalline form and response to the Millon reaction, leucin and alanin by the appearance and analysis of their copper derivatives, glycocoll by the f. p. (156°), crystalline form and nitrogen content of its β -naphthalenesulfo compound, and arginin by the crystalline form and f. p. (225°) of its pierolonate.

In a case of cystinuria tyrosin and leucin have been found in the urine, the former identified by its crystalline form, response to the Millon reaction and C and H content, the latter by the f. p. (67°) and analysis of its β -naphthalenesulfo compound.

The separation and identification of amido acids is now usually made by Fischer and Bergell's method, or one of its modifications, which depends upon the fact that amido acids enter into reaction in presence of alkalies with β -naphthalenesulfochlorid to form crystalline, difficultly soluble compounds, of the type of β -naphthalenesulfoglycin: $C_{10}H_7.SO_2.HN.CH_2.COOH$, which correspond in structure to hippuric acid and other benzoyl, etc., derivatives of amido acids (p. 480). Another method of separation of amido acids, devised by Fischer, consists of their conversion into their esters, and the fractional distillation of these. The details of these methods are too intricate to be considered here.

Cystin— α -diamido— β -dithiodilactic acid—was first obtained from a rare form of urinary calculus (p. 759), and has since been shown to be identical with the cystin obtained by hydrolysis of proteins

(p. 421, 580), it having been demonstrated that "calculus cystin" and "protein cystin" are not two isomeric forms, but one and the same substance. Cystin occurs in the normal urine in small quantity, and is greatly increased in amount in the uncommon condition of **cystinuria**, when it forms yellowish sediments in the urine, containing its characteristic crystals (Fig. 46). The quantity of cystin produced in this condition is sometimes so great that, by reason of its sparing

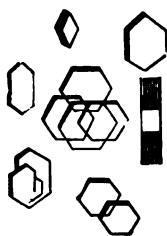


FIG. 46.

solubility, it is deposited in the tissues in sufficient amount to cause death by inanition. In some cases of cystinuria the urine also contains the diamines, putrescin and cadaverin, in others it does not. Leucin and tyrosin have been found to accompany cystin in one case of cystinuria, and it seems probable that the substance described as "calculus cystin" was tyrosin. Several cases of cystinuria have been carefully studied from the chemical standpoint in recent

years, but the investigations have led to little definite knowledge of the chemism of this obscure form of disturbance of protein metabolism.

Cystin is best separated from the urine and determined by precipitation with benzoyl chlorid by Baumann and Goldmann's method, or, less exactly, by precipitation by strong acidulation with acetic acid and purification of the precipitate by reprecipitation from a solution in ammonia.

URINARY CALCULI.

Urinary calculi, or concretions, may be formed in any part of the urinary tract, but are most frequently formed in the pelvis of the kidney or in the bladder. They are usually single, but may be multiple, as many as 300 having been found in the bladder at one time. When multiple, their surfaces are usually polished and formed into facets by mutual attrition. They vary in size from mere gravel to masses as large as a hen's egg, and weighing as much as 1,500 gms. Calculi, other than phosphatic and ammonium urate concretions, are usually composed of the same material throughout, constituting "primary deposits." Phosphatic, ammonium urate, and, very rarely, calcium carbonate calculi are produced as "secondary deposits," being formed in an alkaline or subacid urine, as a so-called "crust," which frequently constitutes almost the entire mass of the stone, by deposition upon a "nucleus," or nuclei, consisting either of a primary deposit or of some foreign substance. The constituents of urinary calculi most frequently met with are uric acid, sodium urate, ammonium urate, calcium oxalate, calcium phosphate and ammonio-magnesian phosphate: those of rarer occurrence are cystin, xanthin.

urates of potassium, calcium and magnesium, and calcium carbonate. Of very exceptional occurrence are calculi of indigo, silica, fatty acids (urostealiths), and bilirubin (hæmatoidin).

Uric acid calculi are usually small in size, and of renal origin, although they are met with as vesical calculi of great size. They are always produced in a strongly acid, concentrated urine. They are gray, brownish-yellow or reddish-brown in color, sometimes smooth-surfaced, but usually finely nodulated, and quite hard. They are almost always primary, although occasionally uric acid forms alternate layers with calcium oxalate in a composite stone.

Ammonium urate is sometimes met with as a primary deposit in renal calculi in young children, which are smooth, yellow, oval in section and relatively soft and friable. Much more frequently ammonium urate constitutes a secondary deposit.

Oxalate calculi are occasionally small and smooth, more usually very rough and coarsely nodulated, very hard, and varying in color from very pale yellow to dark-brown. They are known as "mulberry calculi" from their shape.

Phosphatic calculi are almost invariably secondary deposits, and consist usually of a mixture of calcium phosphate, ammonio-magnesian phosphate and ammonium urate. They may attain great size, are always rough-surfaced, white to yellowish or pink in color, and relatively soft and friable. Calculi whose predominating constituent is ammonio-magnesian phosphate are called "fusible calculi."

Cystin calculi, although rarely met with, are of more frequent occurrence than the other "rare" forms. They are primary, yellow, smooth or rough, of crystalline structure throughout, consisting entirely of cystin, quite soft, and usually small, although they have been known to attain the size of an egg. Xanthin calculi are of very rare occurrence. They are primary, and consist either entirely of xanthin, or of xanthin and uric acid. They vary in color from pale yellow to brown, and are sometimes as large as a pigeon's egg. Urates of potassium, calcium and magnesium are occasionally met with in urate calculi, never as the sole constituents. Calcium carbonate, while frequently met with as a secondary deposit in calculi of large size in the lower animals, is very rarely found in the human subject, in the crust of a calculus formed with a foreign body as a nucleus or in a siliceous calculus. Urostealiths consist either entirely of fatty acids with a little phosphate, or are covered with a crust of phosphates, produced as a secondary deposit. In the former case they are of the consistency of India-rubber when moist, but become hard and brittle when dry. Only five such calculi have been described. Indigo was found to be one constituent of a calculus weighing 40 gms. formed in the pelvis of a kidney. Blue crystals

of indigo have also been met with inclosed in oxalate calculi. Silica calculi are extremely rare. The author has seen the nucleus of a phosphatic calculus consisting entirely of silica and an oxid of iron. An oxalate calculus has been found to contain crystals of hæmatoidin.

For the chemical examination of calculi the stone should be sawed in two; the sawdust affording sufficient material for chemical examination. The sawdust from the central portions of the calculus should be collected and examined separately from that derived from the crust. The following scheme of analysis will be found useful for the examination of calculus dust, a separate portion of the material being used for each operation, except where otherwise directed :

SCHEME FOR DETERMINING THE COMPOSITION OF URINARY CALCULI.

1. Heat a portion on platinum foil :
 - a. It is entirely volatile 2
 - b. A residue remains 5
2. Moisten a portion with HNO_3 ; evaporate to dryness at low heat; add NH_4HO :
 - a. A red color is produced 3
 - b. No red color is produced 4
3. Treat a portion with KHO , without heating :
 - a. An ammoniacal odor is observed *Ammonium urate.*
 - b. No ammoniacal odor *Uric acid.*
4. a. The HNO_3 solution becomes yellow when evaporated; the yellow residue becomes reddish-yellow on addition of KHO , and, on heating with KHO , violet-red *Xanthin.*
 b. The HNO_3 solution becomes dark brown on evaporation, *Cystin.*
5. Moisten a portion with HNO_3 ; evaporate to dryness at low heat; add NH_4HO :
 - a. A red color is produced 6
 - b. No red color is produced 9
6. Heat before the blow-pipe on platinum foil :
 - a. Fuses 7
 - b. Does not fuse 8
7. Bring into blue flame on platinum wire :
 - a. Colors flame yellow *Sodium urate.*
 - b. Colors flame violet *Potassium urate.*

8. The residue from 6:
 - a. Dissolves in dil. HCl with effervescence; the solution forms a white ppt. with ammonium oxalate *Calcium urate*.
 - b. Dissolves with slight effervescence in dil. H_2SO_4 ; the solution, neutralized with NH_4HO , gives a white ppt. with HNa_2PO_4 ,
Magnesium urate.
9. Heat before the blow-pipe on platinum foil:
 - a. It fuses *Ammonio-magnesian phosphate*.
 - b. It does not fuse 10
10. The residue from 9, when moistened with H_2O , is:
 - a. Alkaline 11
 - b. Not alkaline *Tricalcic phosphate*.
11. The original substance dissolves in HCl:
 - a. With effervescence *Calcium carbonate*.
 - b. Without effervescence *Calcium oxalate*.

MILK

As the milk of the cow has been the best studied, and as it is an important article of food, it will be first considered, and the difference between it and human milk will be subsequently referred to.

Physical Properties.—Milk is white, yellowish, or, in thin layers, or if diluted with water, bluish. It is opaque, the opacity being due to the fact that it is an emulsion, and that light is extinguished by the repeated refractions in passing between the watery liquid and the oil globules. Consequently, the richer the milk is in fat, the thinner the layer in which it is capable of causing a certain degree of extinction of light; a fact which is utilized in some forms of "milk-testers." The odor of milk is faint, but characteristic, and its taste is sweetish.

Its reaction when fresh is amphoteric, the mean alkalinity being equivalent to 41 cc. N/10 NaHO for 100 cc. milk (phenolphthaleïn), and its mean acidity equivalent to 19.5 cc. N/10 H_2SO_4 . In air the reaction soon turns to acid, by reason of formation of lactic and succinic acids from the milk-sugar by micro-organisms, a change which takes place during the "souring" of milk, and has an influence upon the action of heat upon it. Fresh milk does not coagulate upon boiling, even after treatment with carbon dioxid. As it gradually sours, it first coagulates on boiling after treatment with CO_2 ; then on boiling alone; at a later stage it coagulates by the action of CO_2 at the ordinary temperature; and, finally, it coagulates spontaneously, without CO_2 or heat, expressing a yellowish liquid, the **whey**. This

change is due to bacterial action, and may be prevented by sterilizing the milk by heat, or by antiseptics.

The specific gravity of cow's milk varies from 1027 to 1035, being higher with skimmed milk, and lower with very rich milk and with watered milk. The lactometer is simply a specially graduated spindle by which the sp. gr. of the milk is determined, and milk having a sp. gr. below 1027 is considered as adulterated. It must be remembered, however, that as the specific gravity is raised by skimming and lowered by watering, the original sp. gr. may be maintained by practicing both forms of adulteration to suitable degrees; and also that very rich milk has a lower sp. gr. than that less rich in cream. Therefore, the lactometer can only be relied upon when used in connection with the creamometer, or other means of determining the proportion of fat. The average sp. gr. of good cow's milk is 1030, and the percentage of cream 13.

Composition.—Milk consists of a watery solution of proteins, lactose and mineral salts, sometimes called the **plasma**, which holds in suspension minute globules of fat, sometimes called the **corpuscles**. On standing, the fat rises, more or less completely, to the surface, forming a layer much richer in fat than the milk, which is the **cream**, upon removal of which the **skim-milk** remains. The separation of fat is more rapidly and completely effected by **cream-separators**, which are centrifugal machines adapted to this purpose. The "corpuscles," which contain all the fat of the milk, number from 1 to $5\frac{1}{2}$ million per cc., and are from .0024 to .0046 mm. in diameter. It is probable that the fat-globules of milk are enclosed in an envelope, because, unless the milk have been previously treated with alkali, agitation with ether does not readily extract the fat, and also because the globules are stained by certain agents which do not stain fats. Besides fat, the globules contain small quantities of lecithins, cholesterol, and a yellow coloring-matter. The fat of milk, **butter-fat**, is more complex in composition than other fats and oils, from which it differs particularly in containing a larger proportion of the glycerids of the lower, volatile, fatty acids, a fact which is taken advantage of for the detection of adulterations of butter. Milk-fat, when saponified, yields about 94% of fatty acids, of which 86 to 89% consists of insoluble, non-volatile acids, palmitic, stearic and oleic, with minute quantities of caprylic, capric, lauric and arachic acids (p. 333), the oleic acid constituting from $\frac{3}{10}$ to $\frac{4}{10}$ of the whole. The remaining 5 to 8% consist of soluble, volatile acids, butyric ($\frac{2}{3}$ to $\frac{4}{3}$) and caproic ($\frac{2}{3}$ to $\frac{4}{3}$). Other fats and oils yield only mere traces of volatile, soluble acids on saponification. Whether these acids exist in milk and butter as separate glycerids, such as tributyrin, $C_3H_5(C_4H_7O_2)_3$, tripalmitin, $C_3H_5(C_{16}H_{31}O_2)_3$, and tristearin, $C_3H_5(C_{18}H_{35}O_2)_3$, or as mixed glycerids, such as $C_3H_5(C_4H_7O_2)(C_{16}H_{31}O_2)(C_{18}H_{35}O_2)$, is unknown.

Butter.—Good, natural butter contains 80 to 90% of butter-fat, 6 to 10% of water, 2 to 5% of curd (casein), 2 to 5% of salt, and, almost always, some artificial "butter-color." About the only adulteration of butter now practiced is by admixture of other animal fats (beef or mutton tallow), and vegetable or animal oils (cotton-seed or lard-oil), or by substitution of imitation butter. **Oleomargarine** is a product made in imitation of butter, which it resembles very closely in color, taste, odor, and general appearance. It is made from beef-fat, which is hashed, steamed, and subjected to pressure at a carefully regulated temperature. Under this treatment it is separated into two fatty products, one a white solid, "stearin," the other a faintly yellow oil, "oleo-oil." This oil is then mixed with milk, and the remaining steps in the manufacture are the same as in making butter from cream. "Butterine," "suine," etc., are products made, by modifications of the above process, from beef or mutton-tallow, lard and cotton-seed oil.

Milk-plasma—the liquid portion of the milk remaining after complete removal of the fat-globules, contains the dissolved constituents. These consist of at least three proteins: Caseinogen, the parent substance from which the casein is derived, lactalbumin, and lactoglobulin; two carbohydrates, milk sugar and dextrine-like substance; mineral salts; and small quantities of lecithins, nuclein, cholesterol, urea, creatin, creatinin, and calcium citrate.

Casein—is the protein produced from the caseinogen of milk by the coagulating action of the rennet from the stomach of the calf. Probably the caseinogens, and the caseins derived therefrom, in the milk of different kinds of animals are not identical with each other. That from human milk and that from the milk of the cow differ in the form of the coagulum, in solubility in acids, and in the nature of the products of decomposition. The casein of cow's milk is a nucleoalbumin, and, on digestion with pepsin and hydrochloric acid, leaves a pseudonuclein, which is not the case with the casein from human milk. It contains 0.8% of sulfur, and 0.85% of phosphorus. By hydrolysis of cows' milk a number of monamido and diamido acids have been obtained: tyrosin, leucin, glycocoll, alanin, phenyl-alanin, aspartic acid, glutamic acid, prolin, arginin, lysin, and a diamido acid having the empirical formula $C_{12}H_{26}N_2O_5$, which is a diamidotrioxydodecan acid. Casein, which is the principal protein of cheese, is, when dry, a white powder, very sparingly soluble in water and in solutions of neutral salts, except that it is somewhat soluble in 1 per cent solutions of sodium fluorid or of potassium or ammonium oxalate. It behaves as an acid towards alkaline solutions, in which it

dissolves, forming solutions which may be neutral or even acid, if the proportion of alkali be small. It expels carbon dioxid from calcium carbonate, and forms a soluble compound with calcium phosphate. Its solutions do not coagulate by heat. Addition of a very small quantity of dilute hydrochloric or acetic acid causes precipitation of casein from its solutions, less readily in the presence of neutral salts; the precipitate dissolving readily in an excess of the acid, and being again produced by marked excess of mineral acids. Neutral solutions are precipitated by salting with sodium chlorid or magnesium sulfate, and by solutions of alum, or of zinc or copper salts. The most notable property of caseinogen is its coagulation (conversion into casein or paracasein) by the action of rennet, in the presence of calcium salts.

On digestion with pepsin-hydrochloric acid, cow's casein dissolves, leaving a residue of a nucleoalbumin, whose quantity and whose phosphorus-content vary. Indeed, with a large excess of pepsin-hydrochloric acid, no residue remains. By tryptic digestion the phosphorus is split off, in part as phosphoric acid, and in part in organic combination.

Casein may be obtained from milk by dilution with four volumes of water, precipitation by addition of acetic acid to 1 p/m, repeated resolution in dilute alkali and reprecipitation by acetic acid, washing with water, drying, and washing with alcohol, and finally with ether.

Lactalbumin—is a protein containing no phosphorus, and 1.73% of sulfur. It has the properties of the albumins, and resembles serum albumin, having about the same coagulation-temperature, 72° to 84° , varying with the proportion of salts present, but having a lower specific rotary power: $[\alpha]_D = -37^{\circ}$. It may be separated from milk, after removal of lactoglobulin and casein by salting with magnesium sulfate, by precipitation with acetic acid.

Lactoglobulin—closely resembling, if not identical with serum globulin, is a protein precipitable from milk, after removal of casein by salting with sodium chlorid, by saturation with magnesium sulfate.

Lactose—see p. 318.

Mineral salts—exist in cow's milk in the proportion of about 0.7%. They consist of the chlorids and phosphates of sodium, potassium, calcium and magnesium, and traces of iron.

Human milk—differs from cow's milk principally in the proportion of the several constituents, and in the nature of the proteins. The composition of cow's milk and of human milk is given by König as follows:

	Cow's Milk			HUMAN MILK		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Water	87.41	80.32	91.50	87.21	83.69	90.90
Total solids	11.59	8.50	19.68	12.71	9.10	16.31
Fat	3.66	1.15	7.09	3.78	1.71	7.60
Milk-sugar	4.92	3.20	5.67	6.04	4.11	7.80
Casein	3.01	1.17	7.40	1.03	0.18	1.90
Albumin	0.75	0.21	5.04	1.26	0.39	2.35
Proteins	3.76	1.38	12.44	2.29	0.57	4.25
Ash	0.70	0.50	0.78	0.31	0.14	†

Therefore, in human milk the proportion of proteins is less, and that of sugar greater than in cow's milk.

The casein of human milk is, apparently, not a nuclealbumin, at all events it leaves no residue of pseudonuclein on digestion with pepsin-hydrochloric acid. It does, however, contain phosphorus in somewhat less proportion than cow's casein, 0.68%. It is coagulated incompletely by rennet in fine, separate flocculi, while cow's casein is coagulated by rennet in dense, curdy masses. Human casein is more difficultly precipitated by acids than cow's casein, and is more readily soluble in slight excess of the acid. These differences are not due to differences in the nature or amount of the salts present, but to differences in the proteins themselves, which also differ in their chemical composition, human casein containing less carbon, nitrogen and phosphorus than cow's casein, and more hydrogen, oxygen and sulfur. The spontaneous coagulation of human milk on exposure to air at the ordinary temperature takes place more slowly than that of cow's milk. The quantity of proteins in human milk is notably greater early in lactation than later, being as high as 3 p/m in the earlier stages. The proportion of milk-sugar, on the contrary, increases with the duration of lactation.

Besides caseinogen, lactalbumin and lactoglobulin, human milk contains another protein, **opalisin**, which contains a large proportion of sulfur, 4.7%.

Abnormal Milk.—It will be seen by the table given above that the proportion of fat, sugar and proteins in both cow's milk and human milk vary within quite wide limits. A milk containing less than the minimum of these constituents there given is certainly abnormal, and one containing no more than the mean is of inferior quality. The New York state dairy law declares any milk found on analysis to contain "less than 12% of milk solids, which shall contain not less than 3% of fat" to be adulterated. These limits are fixed upon the assumption, based upon a great number of analyses,

that a milk falling below the requirements, if not fraudulently adulterated, is the product of cows kept under improper hygienic conditions, or diseased. The quality of milk, whether of women or of cows, is affected by the physical condition of the individual, the nutrition, and the composition of the food, the duration of lactation, and the mental emotions. The last-named influence the quality of the milk much more seriously than is generally appreciated. The milk of cows which are harassed or excited has been found to be much more liable to cause alimentary disturbances in infants than that obtained from animals which are gently treated and kept free from excitement. It is also well known that the milk of women during violent mental excitement may become absolutely poisonous to the nursing infant.

Cow's milk has been frequently the medium of transmission of disease. Bacteria are found in the freshly-drawn milk of cows affected by disease, and it has been stated that tuberculosis may thus be transmitted from the cow to the human subject. Less open to question is the transmission of diphtheria, scarlet fever, and, particularly, typhoid, by contamination of the milk by exposure to the air, or by admixture of contaminated water, particularly as milk is an excellent nutrient material for bacteria. The physical qualities of milk are also sometimes modified by bacterial action, the milk becoming bitter in taste, or ropy in consistency, or red or blue in color.

Medicinal and poisonous substances taken by the mother may pass into the milk in quantity sufficient to cause serious effects upon the nursing infant. Thus infants are frequently narcotized by opiates taken by the mother, and at least two instances of fatal poisoning by this means have been reported.

The adulteration of milk now is practically limited to the addition of water, or the removal of cream, or both.

Analysis of Milk.—The constituents of milk usually determined in milk analysis are: total solids (milk-solids), fat, solids not fat, and ash. A simple method, and one giving sufficiently accurate results, is that of Sharples: ten cc. of the milk are measured out into a weighed, flat platinum dish (milk-dish), and weighed. The difference between this weight and that of the dish is the weight of milk used. The dish is then placed on the water-bath until the milk is evaporated to dryness, heated for half an hour in an air-oven at 105°, cooled and weighed. This weight, minus the weight of the dish, is the weight of milk-solids in the weight of milk used. The dish is then filled with petroleum-ether (obtained by distilling gasoline on the water-bath), which is poured off from the solid residue, which usually adheres firmly to the dish; and the treatment

with petroleum-ether repeated six times. The residue is heated for a few minutes in the air-oven, cooled, and weighed. This weight, minus that of the empty dish, is that of the solids not fat; and, subtracted from the weight of milk-solids, gives the weight of fat in the amount of milk used. The residue is then burnt to a white ash, cooled and weighed, giving the amount of ash.

The extraction of fat by the above method is not complete, and therefore the determination of fat is affected with a slight minus error. When more accurate determination of fat is desired, Adams' method is to be preferred: strips of thin blotting-paper about 50 cent. long and 6 cent. wide, which have been freed from fat by extraction with ether and with alcohol, dried and weighed, along with the platinum wire below referred to, are used. The milk sample is placed in a small wash-bottle, which is then weighed. One of the paper strips is suspended in a horizontal position, and from 8 to 10 cc. of the milk are distributed over it from the wash-bottle, which is then reweighed to determine the amount of the sample used. When the milk upon the paper strip has become air-dried, the strip is coiled into a spiral, about which the platinum wire is fastened, and which is then dried in an air-oven at 105° . When dry, the spiral is cooled and weighed, to determine the total solids, and then extracted with ether in a Soxhlet extractor. The fat is determined by evaporation of the ether extract, and weighing the residue.

Of the more rapid, physical methods of fat-determination probably the most satisfactory is that of Babcock: The milk is mixed with an equal volume of sulfuric acid, transferred to a small bottle having a long, thin, graduated neck, constructed for the purpose, and centrifugated. The percentage of fat is read off on the graduation.

For the determination of total proteins and sugar in the same sample, Ritthausen's method is generally used: 25 gm. of the milk are diluted with water to 400 cc., 10 cc. of a solution of CuSO_4 containing 6.5 gm. to the litre, and a solution of KHO (14.2 gm. to the litre), or of NaHO (10.2 gm. to the litre) are added so that the reaction remains faintly acid or neutral (it must not become alkaline). When the precipitate of proteins has formed, 100 cc. of water are added, the mixture is stirred and filtered through a small filter of known nitrogen-content. The filtrate is used for the sugar determination: 100 cc. are added to 50 cc. of boiling Fehling's solution, and the determination is concluded as usual. The protein coagulum is washed, by decantation and upon the filter, with water, and the proportion of nitrogen is determined in the filter and precipitate by Kjeldahl's method. The nitrogen found, multiplied by 6.37, gives the protein-content.

APPENDIX.

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APPENDIX A.

ORTHOGRAPHY AND PRONUNCIATION OF CHEMICAL TERMS.

In 1887 a committee was appointed by the American Association for the Advancement of Science, to consider the question of securing uniformity in the spelling and pronunciation of chemical terms. The work of this committee extended through the four following years. As a result of widespread correspondence and detailed discussion at the annual meetings of the Chemical Section of the American Association, the following rules have been formulated and adopted by the Association.

A circular embodying the substance of these rules has been issued by the Bureau of Education at Washington, and distributed among chemists and teachers of chemistry, with a recommendation of their general adoption.

GENERAL PRINCIPLES OF PRONUNCIATION.

1. The pronunciation is as much in accord with the analogy of the English language as possible.
2. Derivatives retain as far as possible the accent and pronunciation of the root word.
3. Distinctly chemical compound words retain the accent and pronunciation of each portion.
4. Similarly sounding endings for dissimilar compounds are avoided, hence -In, -Id, -ite, -äte.

ACCENT.

In polysyllabic chemical words the accent is generally on the antepenult; in words where the vowel of the penult is followed by two consonants, and in all words ending in -ic, the accent is on the penult.

PREFIXES.

All prefixes in strictly chemical words are regarded as parts of compound words, and retain their own pronunciation unchanged (as ä'ceto-, ä'mido-, ä'zo-, hÿ'dro-, í'so-, nī'tro-, nītrō'so-).

ELEMENTS.

In words ending in -ium, the vowel of the antepenult is short if i (as *irí'dium*), or y (as *dídý'mium*), or if before two consonants (as *că'leium*), but long otherwise (as *títā'nium*, *sělē'nium*, *chrō'mium*).

alū'minium	e'rbium	me'reury	sō'dium
a'ntimony	fū'orin	mōlý'bdenum	strō'ntium
a'rsēnic	gā'llium	n'ekel	(sbium)
bā'rium	germā'nium	n'trogen	sū'lfur
bi'smuth (biz)	glā'cinum	ō'smium	tā'ntalum
bō'ron	gold	ō'xygen	tellū'rium
brō'mīn	hý'drogen	pallā'dium	te'rbium
cā'dmium	í'ndium	phōs'phorus	thā'llium
cā'leium	í'odin	plā'tinum	thō'rium
ca'rbon	irí'dium	potā'ssium	tin
cō'rium	iron	rhō'dium	títā'nium
cō'sium	lā'nthanum	rubí'dium	tū'ngsten
chlō'rīn	lead	ruthē'nium	ū'rā'nium
chrō'mium	lī'thium	samā'rium	vā'nā'dium
cō'balt	magnē'sium	scā'ndium	ytte'rbium
colū'mbium	(zhium)	sēlē'nium	ý'ttrium
co'pper	ma'nganese	el'licon	zinc
dídý'mium	(eze)	silver	zircō'nium

Also: āmmō'nium, phosphō'nium, hā'logen, cýā'nogen, āml'-dogen.

Note in the above list the spelling of the halogens, cesium and sulfur; f is used in the place of ph in all derivatives of sulfur (as sulfuric, sulfite, sulfo-, etc.).

TERMINATIONS IN -ic.

The vowel of the penult in polysyllables is short (as *cýā'nic*, *fūmā'ric*, *arsē'nic*, *silí'cic*, *īō'dic*, *būtý'ric*), except (1) u when not used before two consonants (as *mercū'ric*, *prū'ssic*), and (2) when the penult ends in a vowel (as *benzō'ic*, *olē'ic*); in dissyllables it is long except before two consonants (as *bō'ric*, *cí'tric*). Exception: *acē'tic* or *acē'tic*.

The termination -ic, is used for metals only where necessary to contrast with -ous (thus avoid *aluminic*, *ammonic*, etc.).

Fāte, fāt, fār, mēte, mēt, pīne, pīn, marīne, nōte, nōt, mōve, tūbe, tūb, rīle, mý, ý = I.

' Primary accent; " secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

TERMINATIONS IN **ous**.

The accent follows the general rule (as plā'tinous, sū'lfurous, phō'sphorous, cōba'l'tous). Exception: acē'tous.

TERMINATIONS IN **-ate** AND **-ite**.

The accent follows the general rule (as ā'cetāte, vā'nadāte): in the following words the accent is thrown back: ā'bietāte, ā'leoholāte, ā'cetonāte, ā'ntimonīte.

TERMINATIONS IN **-id** (FORMERLY **-ide**).

The final **e** is dropped in every case and the syllable pronounced **id** (as chlō'rīd, ī'odīd, hŷ'drīd, ō'xīd, hŷdrō'xīd, sū'līd, ā'mīd, ā'nīlīd, mūrē'xīd).

TERMINATIONS IN **-ane**, **-ene**, **-ine**, AND **-one**.

The vowel of these syllables is invariably long (as mē'thāne, ē'thāne, na'phthalēne, a'nthracēne, prō'pīne, quī'nōne, ā'cetōne, kē'tōne).

A few dissyllables have no distinct accent (as benzēne, xŷlēne, cētēne).

The termination **-ine** is used only in the case of doubly unsaturated hydrocarbons, according to Hofmann's grouping (as propīne).

TERMINATIONS IN **-in**.

In names of chemical elements and compounds of this class, which includes all those formerly ending in **-ine** (except doubly unsaturated hydrocarbons), the final **e** is dropped, and the syllable pronounced **-in** (as chlō'rīn, brō'mīn, etc., ā'mīn, ā'nīlīn, mo'rphīn, quī'nīn (kwī'nīn), vanī'llīn, alloxā'ntīn, absi'nthīn, emŷ'lsīn, cā'ffeīn, cō'caīn).

TERMINATIONS IN **-ol**.

This termination, in the case of specific chemical compounds, is used *exclusively* for alcohols (and phenols, W.), and when so used is

Fāte, fāt, fār, mēte, mēt, pīne, pīn, marīne, nōte, nōt, mōve, tūbe, tūb, rūle, mŷ, ŷ = I.

' Primary accent; " secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

never followed by a final *e*. The last syllable is pronounced -ōl (as gly'cōl, phē'nōl, crē'sōl, thȳ'mōl (ti), glȳ'cerol, quī'nōl.)
 Exceptions: ā'lcōhōl, a'rgōl.

TERMINATIONS IN -ole.

This termination is always pronounced -ōle, and its use is limited to compounds which are not alcohols (or phenols, W.) (as ĩ'ndōle).

TERMINATIONS IN -yl.

No final *e* is used; the syllable is pronounced ŷl (as ā'cetŷl, ā'mŷl, cē'rotŷl, cē'tŷl, ē'thŷl).

TERMINATIONS IN -yde.

The *y* is long (as ā'ldehȳde).

TERMINATIONS IN -meter.

The accent follows the general rule (as hydrō'meter, barō'meter, lactō'meter). Exception: words of this class used in the metric system are regarded as compound words, and each portion retains its own accent (as cē'ntime''ter, mī'llime''ter, kī'lome''ter).

MISCELLANEOUS WORDS WHICH DO NOT FALL UNDER THE PRECEDING RULES.

Note the spelling: albumen, albuminous, albuminiferous, asbestos, gramme, radical.

Note the pronunciation: ā'lkalīne, ā'lloy (n. and v.), ā'llotropy, ā'llotropism, ĩ'somerism, pō'lymerism, apparā'tus (sing. and plu.), āqua regia, barȳ'ta, cēntigrade, co'ncentrated, crystallīn or crystallīne, electrō'lysis, liter, mō'lecule, mōlē'cular, nō'menclā''ture, olē'fiant, vā'lence, ū'nivā''lent, bī'vā''lent, trī'vā''lent, qua'drivā''lent, tī'trate.

Fāte, fāt, fār, mēte, mēt, pīne, pīn, marīne, nōte, nōt, mōve, tūbe, tūb, rūle, mŷ, ŷ=ĭ.

' Primary accent; '' secondary accent. N. B.—The accent follows the vowel of the syllable upon which the stress falls, but does not indicate the division of the word into syllables.

A LIST OF WORDS WHOSE USE SHOULD BE AVOIDED IN FAVOR OF
THE ACCOMPANYING SYNONYMS.

<i>For—</i>	<i>Use—</i>
sodic, calcic, zincic, nickelic, etc., chlorid, etc.	sodium, calcium, zinc, nickel, etc., chlorid, etc. (vid. terminations in -ic supra).
arsenetted hydrogen	arsin
antimonetted hydrogen	stibin
phosphoretted hydrogen	phosphin
sulfuretted hydrogen, etc.	hydrogen sulfid, etc.

<i>For—</i>	<i>Use—</i>
beryllium	glucinum
niobium	columbium
glycerin	glycerol
hydroquinone (and hydrochinon)	quinol
pyrocatechin	catechol
resorcin, etc.	resorcinol, etc.
mannite	mannitol
dulcite, etc.	dulcitol, etc.
benzol	benzene
toluol, etc.	toluene, etc.
thein	caffein

<i>For—</i>	<i>Use—</i>
furfurol	furfuraldehyde
fucusol	fucusaldehyde
anisol	methyl phenate
phenetol	ethyl phenate
anethol	methyl allylphenol
alkylogens	alkyl haloids
titer (n.)	strength or stand- ard
titer (v.)	titrate
monovalent	univalent
divalent, etc.	bivalent, etc.
quantivalence	valence

APPENDIX B.—TABLES.

TABLE I.—SOLUBILITIES.

FRESNIUS.

W or w=soluble in H₂O. A or a=insoluble in H₂O; soluble in HCl, HNO₃, or aqua regia. I or i=insoluble in H₂O and acids. W-A=sparingly soluble in H₂O, but soluble in acids. W-I=sparingly soluble in H₂O and acids. A-I=insoluble in H₂O, sparingly soluble in acids. Capitals indicate common substances.

	Aluminium.	Ammonium.	Antimony.	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper.	Ferrous.	Ferric.
Acetate . . .	W	W	. .	W	w	W	W	w	W	W	W	W
Arsenate . . .	a	w	a	a	a	a	a	a	a	a	a	a
Arsenite . . .	. .	w	a	a	. .	a	. .	. .	a	A	a	a
Benzoate . . .	W	W	. .	w	. .	W	W	. .	. .	a	W	a
Borate . . .	a	w	. .	a	a	W-A	a	a	a	a	a	a
Bromid . . .	W	W	W-A	w	W-A	W	W	W-I	a	W	W	W
Carbonate . . .	a	W	. .	A	A	a	A	a	A	A	A	a
Chlorate . . .	W	w	. .	W	w	W	W	W	W	W	W	W
Chlorid . . .	W	W ²	W-A ⁶	W	W-A ¹⁰	W	W	W-I	W	W	W	W
Chromate . . .	. .	w	a	a	a	a	W-A	a	a	w	w	W
Citrate . . .	W	W	. .	a	. .	a	W-A	w	W	W	W	W
Cyanid . . .	. .	W	. .	W-A	. .	a	W	a	a-I	a	a-I	. .
Ferrieyanid . . .	. .	w	. .	. .	. .	. .	W	. .	i	. .	I	w
Ferrocyanid . . .	. .	w	. .	W-A	. .	. .	W	. .	i	i	i	I
Fluorid . . .	W	W	w	a-I	w	W-A	A	w	W-A	a	W-A	w
Formate . . .	W	W	. .	w	w	W	W	w	W	W	w	W
Hydrate . . .	A	W	A	W	a	a	W-A	A	A	a	a	A
Iodid . . .	W	W	W-A	w	a	W	w	w	W	w	W	w
Malate . . .	W	W	. .	W-A	. .	. .	W-A	. .	. .	. .	. .	W
Nitrate . . .	W	W	. .	W	W ¹¹	w	w	W	W	W	W	W
Oxalate . . .	a	W	a	a	a	a	A	W-A	A	a	a	a
Oxid . . .	A-I	. .	a ⁷	W	a	a	W-A	A-I	A	A	a	A
Phosphate . . .	a	W ³	W-A	W-A	a	a	W-A	a	a	a	a	a
Silicate . . .	A-I	. .	. .	. .	. .	a	a	a	a	a	a	a
Succinate . . .	W-A	W	. .	W-A	. .	W	W-A	. .	W-A	W-A	w	. .
Sulfate . . .	W ¹	W ⁴	a	A	w	W	W-I	W-A ¹²	W ¹³	W	W	W
Sulfid . . .	a	W	A ⁸	W	a	A	W-A	a-i	a	A	A	A
Tartrate . . .	W	W ⁵	a ⁹	a	a	W-A	a	w	W	W	W-A	W ¹⁴

¹(Al₂)(NH₄)₂(SO₄)₄=W; (Al₂)K₂(SO₄)₄=W. ²As(NH₄)Cl₄=W; Pt(NH₄)Cl₅=W-I. ³HNa(NH₄)PO₄=W; Mg(NH₄)PO₄=A. ⁴Fe-(NH₄)₂(SO₄)₂=W; Cu(NH₄)₂(SO₄)₂=W. ⁵C₄H₄O₆K(NH₄)=W. ⁶Sb-OC1=A. ⁷Sb₂O₃=soluble in HCl, not in HNO₃. ⁸Sb₂S₃=sol. in hot HCl, slightly in HNO₃. ⁹C₄H₄O₆K(SbO)=W. ¹⁰BiOCl=A. ¹¹(BiO)NO₃=A. ¹²(Cr₂)K₂(SO₄)₄=W. ¹³CoS=easily sol. in HNO₃, very slowly in HCl. ¹⁴(C₄H₄O₆)₄(Fe₂)K₂=W.

TABLE I.—SOLUBILITIES.—Continued.

FRESSENIUS.

W or w=soluble in H₂O. A or a=insoluble in H₂O; soluble in HCl, HNO₃, or aqua regia. I or i=insoluble in H₂O and acids. W-A=sparingly soluble in H₂O, but soluble in acids. W-I=sparingly soluble in H₂O and acids. A-I=insoluble in H₂O, sparingly soluble in acids. Capitals indicate common substances.

	Lead.	Magnesium.	Manganese.	Mercurous.	Mercuric.	Nickel.	Potassium.	Silver.	Sodium.	Strontium.	Stannous.	Stannic.	Zinc.
Acetate . .	W	w	w	w-a	w	w	W	w	W	w	w	w	W
Arsenate . .	a	a	a	a	a	a	W	a	W	a	a	a	. .
Arsenite . .	a	a	a	a	a	a	w	a	w	a	a	. .	. .
Benzoate . .	a	w	w	a	w-a	. .	w	w-a	w	. .	. .	. .	. .
Borate . . .	a	w-a	a	. .	. .	a	W	a	W	a	a	. .	a
Bromid . . .	w-i	w	w	a-i	w	w	W	a	W	w	. .	. .	w
Carbonate . .	A	A	A	a	a	A	W	a	W	A	. .	. .	A
Chlorate . .	w	w	w	w	w	w	W	w	w	w	w	. .	w
Chlorid . . .	W-I	W	W	A-I	W ¹⁶	W	W ²⁰	I	W	W	W	W	W
Chromate . .	A-I	w	w	a	w-a	a	W	a	w	w-a	a	. .	w
Citrate . . .	a	w	a	a	w-a	w	w	a	W	a	. .	. .	w-a
Cyanid . . .	a	w	a	. .	W	a-i	W	i	w	. .	. .	. .	a
Ferricyanid	w-a	w	i	. .	. .	i	W	i	w	. .	. .	. .	a
Ferrocyanid	a	w	a	. .	. .	i	W	i	w	w	. .	. .	a-i
Fluorid . . .	a	a-i	a	. .	w-a	w-a	w	w	w	a-i	w	w	w-a
Formate . . .	w-a	w	w	w	w	w	w	w	w	w	w	. .	w
Hydrate . . .	a	A	a	. .	. .	a	W	. .	W	w	a	a	a
Iodid	W-A	w	w	A	A	w	W	i	w	w	w	w	w
Malate . . .	w-a	w	w	a	w-a	. .	w	w-a	w	w	w	w	w
Nitrate . . .	W	w	w	W	W	W	W	W	W	W	. .	. .	w
Oxalate . . .	a	a	w-a	a	a	a	W	a	W	a	a	w	a
Oxid	A	A	A ¹⁵	A	A	A	W	a	W	W	a	A-I	A
Phosphate . .	a	a ³	a	a	a	a	w	a	W	a	a	a	a
Silicate . . .	a	a	a	. .	. .	a	W	. .	W	a	. .	. .	a
Succinate . .	a	w	w	a	w-a	w	w	a	w	w-a	. .	a	w-a
Sulfate . . .	A-I	W	W	w-a	W ¹⁷	W	W ¹²	W-A	W	I	w	. .	W
Sulfid	A	a	a	a	A ¹⁸	A ¹⁹	W	a ²¹	W	w	a ²²	A ²²	A ²³
Tartrate . .	a	w-a	w-a	w-a	a	a	W	a	w	a	a	. .	a

¹⁵ MnO₂=sol. in HCl; insol. in HNO₃. ¹⁶ Mercurammonium chlorid=A. ¹⁷ Basic sulfate=A. ¹⁸ HgS=insol. in HCl and in HNO₃, sol. in aqua regia. ¹⁹ See 13. ²⁰ PtKCl₅=W-A. ²¹ Only soluble in HNO₃. ²² Sn sulfids=sol. in hot HCl; oxidized, not dissolved, by HNO₃. Sublimed SnCl₄ only sol. in aq. regia. ²³ Easily sol. in HNO₃, difficultly in HCl.

Au₂S=insol. in HCl and in HNO₃, sol. in aq. regia. AuBr₃, AuCl₃, and Au(CN)₃=w; AuI₃=a PtS₂=insol. in HCl, slightly sol. in hot HNO₃; sol. in aq. regia. PtBr₄, PtCl₄, Pt(CN)₄, Pt(NO₃)₄, Pt(C₂O₄)₂, Pt(SO₄)₂=w; PtO₂=a; PtI₄=i.

TABLE II.—WEIGHTS AND MEASURES.

MEASURES OF LENGTH.

1 millimeter	= 0.001 meter	= 0.0394 inch.
1 centimeter	= 0.01 "	= 0.3937 "
1 decimeter	= 0.1 "	= 3.9371 inches.
1 METER		= 39.3708 "
1 decameter	= 10 meters	= 32.8089 feet.
1 hectometer	= 100 "	= 328.089 "
1 kilometer	= 1000 "	= 0.6214 mile.

Inch.	Millimeters.	Inches.	Centimeters.	Inches.	Centimeters.
$\frac{1}{16}$	= 0.3819	2	= 5.08	9	= 22.86
$\frac{1}{8}$	= 0.7637	3	= 7.62	10	= 25.40
$\frac{3}{16}$	= 1.5875	4	= 10.16	11	= 27.94
$\frac{1}{4}$	= 3.175	5	= 12.70	12	= 30.48
$\frac{5}{16}$	= 6.35	6	= 15.24	13	= 45.72
$\frac{3}{8}$	= 12.7	7	= 17.78	14	= 60.96
1	= 25.4	8	= 20.32	16	= 91.44

MEASURES OF CAPACITY.

1 milliliter	= 1 c.c. = 0.001 liter	= 0.0021 U. S. pint.
1 centiliter	= 10 "	= 0.01 "
1 deciliter	= 100 "	= 0.1 "
1 LITER	= 1000 "	= 1.0567 " quart.
1 decaliter	= 10 liters	= 2.6418 " galls.
1 hectoliter	= 100 "	= 26.418 "
1 kiloliter	= 1000 "	= 264.18 "

cu.	in.	cu.	in.	cu.	in.	cu.	in.
1 = 0.06		26 = 1.60		51 = 3.14		7 1/2 = 147.81	
2 = 0.12		27 = 1.66		52 = 3.20		8 = 177.39	
3 = 0.19		28 = 1.73		53 = 3.26		9 = 206.96	
4 = 0.25		29 = 1.79		54 = 3.32		10 = 236.53	
5 = 0.31		30 = 1.85		55 = 3.39		11 = 266.10	
6 = 0.37		31 = 1.91		56 = 3.46		12 = 295.68	
7 = 0.43		32 = 1.98		57 = 3.52		13 = 325.25	
8 = 0.49		33 = 2.04		58 = 3.58		14 = 354.82	
9 = 0.55		34 = 2.10		59 = 3.64		15 = 384.40	
10 = 0.62		35 = 2.16		60 = 3.70		16 = 413.97	
11 = 0.68		36 = 2.22				17 = 443.54	
12 = 0.74		37 = 2.28				18 = 473.11	
13 = 0.80		38 = 2.34				19 = 502.68	
14 = 0.86		39 = 2.40				20 = 532.25	
15 = 0.92		40 = 2.46				21 = 561.82	
16 = 0.99		41 = 2.52				22 = 591.39	
17 = 1.05		42 = 2.58				23 = 620.96	
18 = 1.11		43 = 2.66				24 = 650.53	
19 = 1.17		44 = 2.72				25 = 680.10	
20 = 1.23		45 = 2.77				26 = 709.68	
21 = 1.29		46 = 2.84				27 = 739.25	
22 = 1.36		47 = 2.90				28 = 768.82	
23 = 1.42		48 = 2.96				29 = 798.39	
24 = 1.48		49 = 3.02				30 = 827.96	
25 = 1.54		50 = 3.08				31 = 857.53	

WEIGHTS AND MEASURES

779

WEIGHTS.

1 milligram	= 0.001 gram	= 0.015 grain Troy.
1 centigram	= 0.01 "	= 0.154 " "
1 decigram	= 0.1 "	= 1.543 grains "
1 GRAM		= 15.432 " "
1 decagram	= 10 grams	= 154.324 " "
1 hectogram	= 100 "	= 0.268 lb. "
1 kilogram	= 1000 "	= 2.679 lbs. "

Grains. Grams.

$\frac{1}{16}$	= 0.001
$\frac{1}{8}$	= 0.002
$\frac{1}{4}$	= 0.004
$\frac{1}{2}$	= 0.008
$\frac{1}{1}$	= 0.016
$\frac{1}{2}$	= 0.032
$\frac{1}{1}$	= 0.065
2	= 0.130
3	= 0.194
4	= 0.259
5	= 0.324
6	= 0.389
7	= 0.454
8	= 0.518
9	= 0.583
10	= 0.648
11	= 0.713
12	= 0.778
13	= 0.842
14	= 0.907
15	= 0.972
16	= 1.037
17	= 1.102
18	= 1.166
19	= 1.231
20	= 1.296

Grains. Grams.

21	= 1.361
22	= 1.426
23	= 1.458
24	= 1.555
25	= 1.620
26	= 1.685
27	= 1.749
28	= 1.814
29	= 1.869
30	= 1.944
31	= 2.009
32	= 2.074
33	= 2.139
34	= 2.204
35	= 2.268
36	= 2.332
37	= 2.397
38	= 2.462
39	= 2.527
40	= 2.592
41	= 2.657
42	= 2.722
43	= 2.787
44	= 2.852
45	= 2.916
46	= 2.980

Grains. Grams.

47	= 3.046
48	= 3.110
49	= 3.175
50	= 3.240
51	= 3.305
52	= 3.370
53	= 3.434
54	= 3.499
55	= 3.564
56	= 3.629
57	= 3.694
58	= 3.758
59	= 3.823
60	= 3.888
3	
1	= 3.888
2	= 7.776
3	= 11.664
4	= 15.552
5	= 19.440
6	= 23.328
7	= 27.216
8	= 31.103

3 Grams.

1	= 31.103
2	= 62.207
3	= 93.310
4	= 124.414
5	= 155.517
6	= 186.621
7	= 217.724
8	= 248.828
9	= 279.931
10	= 311.035
11	= 342.138
12	= 373.250
Lbs.	Kilos.
1	= 0.373
2	= 0.747
3	= 1.120
4	= 1.493
5	= 1.866
6	= 2.240
7	= 2.613
8	= 2.986
9	= 3.359
10	= 3.733

1 pound Avdp. = 453.5925 gm.
1 kilo = 2.2046 lbs. Avdp.

TABLE III.

WEIGHT OF ONE CUBIC CENTIMETER OF NITROGEN.

Temperatures in Centigrade.	728	730	732	734	736	738	740	742
	1.1466	1.1498	1.1529	1.1561	1.1593	1.1625	1.1657	1.1689
	1.1415	1.1447	1.1479	1.1511	1.1542	1.1574	1.1606	1.1638
	1.1364	1.1396	1.1428	1.1459	1.1491	1.1523	1.1554	1.1586
	1.1314	1.1345	1.1377	1.1409	1.1440	1.1472	1.1503	1.1535
	1.1263	1.1294	1.1326	1.1357	1.1389	1.1420	1.1452	1.1483
	1.1211	1.1243	1.1274	1.1305	1.1337	1.1368	1.1399	1.1431
	1.1160	1.1191	1.1222	1.1253	1.1285	1.1316	1.1347	1.1378
	1.1107	1.1138	1.1170	1.1201	1.1232	1.1263	1.1294	1.1325
	1.1054	1.1085	1.1117	1.1148	1.1179	1.1209	1.1241	1.1272
Temperatures in Centigrade.	728	730	732	734	736	738	740	742
	1.1601	1.1632	1.1663	1.1694	1.1725	1.1756	1.1787	1.1818
	1.0948	1.0979	1.1009	1.1040	1.1071	1.1102	1.1133	1.1164
	1.0894	1.0924	1.0955	1.0986	1.1017	1.1047	1.1078	1.1109
	1.0839	1.0870	1.0900	1.0931	1.0961	1.0992	1.1023	1.1053
	1.0784	1.0814	1.0845	1.0875	1.0906	1.0936	1.0967	1.0997
	1.0728	1.0758	1.0789	1.0819	1.0849	1.0880	1.0910	1.0940
	1.0671	1.0701	1.0732	1.0762	1.0792	1.0823	1.0853	1.0883
	744	746	748	750	752	754	756	758
	1.1721	1.1753	1.1785	1.1817	1.1848	1.1880	1.1912	1.1944
Temperatures in Centigrade.	744	746	748	750	752	754	756	758
	1.1670	1.1701	1.1733	1.1765	1.1717	1.1829	1.1860	1.1892
	1.1618	1.1649	1.1681	1.1713	1.1744	1.1776	1.1808	1.1839
	1.1566	1.1598	1.1630	1.1661	1.1693	1.1724	1.1756	1.1787
	1.1515	1.1546	1.1577	1.1609	1.1640	1.1672	1.1703	1.1735
	1.1462	1.1493	1.1525	1.1556	1.1587	1.1619	1.1650	1.1681
	1.1409	1.1441	1.1472	1.1503	1.1534	1.1566	1.1597	1.1628
	1.1356	1.1397	1.1419	1.1450	1.1481	1.1512	1.1543	1.1574
	1.1303	1.1334	1.1365	1.1396	1.1427	1.1458	1.1489	1.1520
	1.1248	1.1279	1.1310	1.1341	1.1372	1.1403	1.1434	1.1465
Temperatures in Centigrade.	744	746	748	750	752	754	756	758
	1.1194	1.1225	1.1256	1.1287	1.1318	1.1348	1.1379	1.1410
	1.1139	1.1170	1.1201	1.1231	1.1262	1.1293	1.1324	1.1354
	1.1084	1.1115	1.1145	1.1176	1.1206	1.1237	1.1268	1.1298
	1.1028	1.1058	1.1089	1.1119	1.1150	1.1180	1.1211	1.1241
	1.0971	1.1001	1.1032	1.1062	1.1092	1.1123	1.1153	1.1184
	1.0913	1.0944	1.0974	1.1004	1.1035	1.1065	1.1095	1.1126
	744	746	748	750	752	754	756	758
	1.1721	1.1753	1.1785	1.1817	1.1848	1.1880	1.1912	1.1944
	1.1670	1.1701	1.1733	1.1765	1.1717	1.1829	1.1860	1.1892

Barometric pressure in millimeters.

TABLE III.—Continued.

WEIGHT OF ONE CUBIC CENTIMETER OF NITROGEN.

Temperatures in Centigrade.	760	762	764	766	768	770	772	774
	1.1976	1.2008	1.2040	1.2072	1.2104	1.2136	1.2167	1.2199
	1.1924	1.1956	1.1988	1.2019	1.2051	1.2083	1.2115	1.2147
	1.1871	1.1903	1.1934	1.1966	1.1998	1.2029	1.2061	1.2093
	1.1819	1.1851	1.1882	1.1914	1.1945	1.1977	1.2008	1.2040
	1.1766	1.1798	1.1829	1.1861	1.1892	1.1923	1.1955	1.1986
	1.1713	1.1744	1.1775	1.1807	1.1838	1.1869	1.1901	1.1932
	1.1659	1.1691	1.1722	1.1753	1.1784	1.1816	1.1847	1.1878
	1.1605	1.1636	1.1667	1.1699	1.1730	1.1761	1.1792	1.1823
	1.1551	1.1582	1.1613	1.1644	1.1675	1.1706	1.1737	1.1768
	1.1496	1.1527	1.1558	1.1589	1.1620	1.1650	1.1681	1.1712
	1.1441	1.1472	1.1502	1.1533	1.1564	1.1595	1.1626	1.1657
	1.1385	1.1416	1.1446	1.1477	1.1508	1.1539	1.1569	1.1600
	1.1329	1.1359	1.1390	1.1421	1.1451	1.1482	1.1512	1.1543
	1.1272	1.1302	1.1333	1.1363	1.1394	1.1424	1.1455	1.1485
	1.1214	1.1244	1.1275	1.1305	1.1336	1.1366	1.1396	1.1427
	1.1156	1.1186	1.1216	1.1247	1.1277	1.1307	1.1338	1.1368
	760	762	764	766	768	770	772	774

Temperatures in Centigrade.	776	778	780	782	784	786	788	790
	1.2231	1.2263	1.2295	1.2327	1.2359	1.2391	1.2423	1.2454
	1.2178	1.2210	1.2242	1.2274	1.2306	1.2337	1.2369	1.2401
	1.2124	1.2156	1.2188	1.2219	1.2251	1.2283	1.2314	1.2346
	1.2072	1.2103	1.2135	1.2166	1.2198	1.2229	1.2261	1.2293
	1.2018	1.2049	1.2081	1.2112	1.2144	1.2175	1.2207	1.2238
	1.1963	1.1995	1.2026	1.2057	1.2089	1.2120	1.2151	1.2183
	1.1909	1.1942	1.1973	1.2004	1.2035	1.2067	1.2098	1.2129
	1.1854	1.1885	1.1916	1.1947	1.1979	1.2010	1.2041	1.2072
	1.1799	1.1831	1.1862	1.1893	1.1924	1.1955	1.1986	1.2017
	1.1743	1.1774	1.1805	1.1836	1.1867	1.1898	1.1929	1.1960
	1.1687	1.1718	1.1749	1.1780	1.1811	1.1841	1.1872	1.1903
	1.1631	1.1661	1.1692	1.1723	1.1754	1.1784	1.1815	1.1846
	1.1574	1.1604	1.1635	1.1665	1.1696	1.1727	1.1757	1.1788
	1.1516	1.1546	1.1577	1.1607	1.1638	1.1668	1.1699	1.1729
	1.1457	1.1488	1.1518	1.1548	1.1579	1.1610	1.1640	1.1671
	1.1399	1.1429	1.1459	1.1489	1.1520	1.1550	1.1580	1.1610
	776	778	780	782	784	786	788	790

Barometric pressure in millimeters.

INDEX.

The black figure indicates the page upon which the substance is considered in chief.

- Abrafn, 649.
 Abrin, 573.
 Absolute temperature, 24.
 zero, 24.
 Absorption, 642.
 of gases, 21, 688.
 coefficient of, 688.
 Accipenserin, 589.
 Acenaphthalene, **495**, 500.
 Acetal, 303, **306**, 373.
 acrolein, 310.
 glyceric, 310.
 Acetaldehyde, 302.
 Acetaldoxim, 409.
 Acetals, 306.
 Acetamid, 400, **401**.
 Acetamidin, 388.
 Acetanilid, 455, **475**.
 Acetates, 330.
 Acetenylbenzene, 442.
 Acethæmin, 665.
 Acetochlorhydröse, **368**, 465.
 Acetol, 308, 459.
 salicylate, 459.
 Acetonæmia, 308, 754.
 Acetonamins, 409.
 Acetone, 278, **307**, 428, 442, 543, 625, 719,
 753, 755.
 diethylsulfone, 374.
 dimethylsulfone, 374.
 ethyl-mercaptol, 373.
 phenylhydrazone, 486.
 Acetonitril, 388, 393, **394**, 400, 401.
 Acetonuria, 620, 753.
 Acetophenone, 442, **455**.
 oxim, 455.
 Acetophenyl hydrazid, 486.
 Acetoxim, 382, **409**.
 Acetoxims, 409.
 Acetolulids, 476.
 Acetyl acetone, 512.
 benzene, 455.
 benzoylamin, 569.
 chlorid, 302, 330, **352**, 368, 369, 393, 398,
 400, 410, 455, 457, 475, 486, 499.
 cyanid, 398.
 hydrid, 302.
 hydroxid, 329.
 methylid, 307.
 morphin, 562.
 urea, 406.
 Acetylene, 236, 288, 302, 391, 423, **424**, 433,
 442, 444, 495.
 balids, 426.
 series, 273.
 Acetylids, 425.
 Achroödextrins, **322**, 643.
 Acid (see also Acids).
 acetic, 288, **329**.
 Acid, acetobenzolic, 464.
 acetohydroxamic, 388.
 acetylacetic, 347, 719, **753**, 755.
 acetylamidoacetic, 412.
 acetylpropionic, 347.
 aconitic, 346, **431**.
 acrylic, 331, 342, 427, **428**, 523.
 adenylic, 592.
 adipic, 331, 338.
 Acid albuminates, 582, **590**.
 Acid, allanturic, 515.
 allophanic, 407.
 alloxanic, 515, 527.
 alloxyproteic, 730.
 amidoacetic, 384, 395, 405, 407, 411, 412,
 413, 419, 529, 634 (see Glycocoll).
 amidobenzolic, 456.
 amidocarbonic, 389.
 amidoethylsulfonic, 421.
 amidoformic, 402, 411 (see Acid, Car-
 bamic).
 amidoglutaric, 419.
 amidoguanidinvalerianic, 418 (see Ar-
 ginin).
 amidohydracrylic, 420.
 amidolsethionic, 421, 432, 634 (see
 Taurin).
 amidolsobutylacetic, 414.
 amidolactic, 411, 420.
 amidomalonic, 411, **419**.
 amidooxypropionic, 420.
 amidooxyvalerianic, 420.
 amidophenylacetic, 478.
 amidopropionic, 331, 411, **414**, 523 (see
 Alanin).
 amidosuccinic, 419.
 amidosulfopropionic, 421, 422.
 amidothiohydracrylic, 421.
 amidothiolactic, 421.
 amidothiopropionic, 421.
 amidovalerianic, 580, 581, 589, 595, 617.
 amygdalic, 466.
 amylsulfuric, 293.
 angelic, 429.
 Acid anhydrids, **351**, 410.
 Acid, anilidopropionic, 478.
 anilindisulfonic, 474.
 anilpyroracemic, 481.
 anthranilic, 456, **478**.
 anthraquinonemonosulfonic, 500.
 antitartaric, 344.
 antoxyproteic, 730.
 arachic, 334.
 arsenic, 173, 174.
 arsenious, 172, 173.
 aspartic, 416, **419**, 580, 595, 617, 623,
 686, 763.
 atrolactic, 463.
 atropic, **457**, 463, 553.

- Acid, arivitellic, 586.**
 aselaic, 338.
 barbituric, 526.
 benzenemonosulfonic, 469.
 benzene sulfonic, 440, 444.
 benzene trisulfonic, 469.
 benzhydroxamic, 480.
 benzoic, 413, 418, 440, 441, 453, 456, 458, 468, 479, 480, 492, 493, 606, 725.
 benzoylactic, 464.
 benzoylamidoacetic, 479 (see Acid, hippuric).
 benzoylformic, 463, 464.
 benzoylglycollic, 464.
 benzoylmalonic, 464.
 benzoylpropionic, 724.
 benzoylpyrroacetic, 464.
 benzoyltartronic, 463.
 bismuthic, 210.
 boracic, 187.
 boric, 187.
 brassylic, 338.
 bromic, 135.
 bromomercapturic, 423.
 bromopropionic, 341, 342.
 bromoprotocatechic, 461.
 butylformic, 332.
 butyric, 331, 337, 601, 624.
 cachoutannic, 462.
 caffeic, 462.
 caffeic, 462.
 camphogluconic, 733.
 camphoric, 492.
 camphoronic, 338, 493.
 capric, 333.
 caproic, 332.
 caprylic, 333.
 carbamic, 396, 403, 411, 640.
 carbanillic, 490.
 carbazotic, 472.
 carbolic, 444 (see Phenol).
 carbomandelic, 463.
 carbonic, 340.
 cerotic, 363.
 chelidonic, 517.
 chlorethylsulfonic, 421.
 chloric, 133.
Acid, chlorids, 286.
Acid chlorilactic, 420.
 chloropropionic, 352.
 choleic, 635.
 cholesteric, 635, 638.
 cholic, 634, 636, 639, 640, 680.
 cholonic, 635.
 cholylic, 635.
 chondroitic, 594.
 chondroitinsulfuric, 594, 596, 597, 740.
 chromic, 195.
 chrysophanic, 500.
 cinchomeric, 519, 558.
 cinchoninic, 558, 559.
 cinnamic, 442, 455, 457, 479, 493, 525.
 citraconic, 346, 431.
 citric, 346, 431.
 comenic, 517.
 coumalic, 431.
 cresylic, 446.
 crotonic, 428, 429, 524, 756.
 eumic, 456.
 cyanic, 395, 396.
Acid, cyanoacetic, 337, 395.
 cyanopropionic, 337.
 cyanuric, 396, 404, 407, 408, 530, 537, 715.
 cymenesulfonic, 447.
 cysteic, 423, 640.
 decylic, 333.
 dehydrocholic, 635.
 delphinic, 332.
 deoxycholic, 635.
 dextrolactic, 342.
 dextronic, 343.
 dextrotartaric, 314, 344.
 dialuric, 527.
 diamidoacetic, 416.
 diamidocaproic, 417.
 diamidodithiodilactic, 421, 767.
 diamidopropionic, 417.
 diamidotrioxododecan, 763.
 diamidovalerianic, 417.
 diasobenzene sulfonic, 516.
 dibenzoyldiamidocaproic, 480.
 dibenzoyldiamidovalerianic, 480.
 dibromobenzoic, 461.
 dibromomalonic, 348.
 dibromopropionic, 417.
 dichloroacetic, 330, 346.
 dichromic, 195.
 digallic, 461.
 dihydrocyanic, 399.
 dimalonic, 327, 338.
 dimethoxybenzoic, 565.
 dimethylmalonic, 526.
 dinitronaphtholsulfonic, 498.
 dioxyannamic, 462.
 dioxymalonic, 347.
 diphenic, 499.
 disulfanilic, 474.
 dithiocarbamic, 405.
 dithiodiamidodilactic, 421.
 dithionic, 143.
 elaidic, 430.
 ellagic, 649.
 erythritic, 342.
 erythroglucic, 297, 342.
 ethalic, 333.
 ethidenelactic, 341.
 ethidenemalonic, 431.
 ethidenepropionic, 428.
 ethylacetic, 331.
 ethyldiacetic, 308.
 ethylenelactic, 342.
 ethylene succinic, 418.
 ethylmalonic, 334.
 ethylnitrolic, 376.
 ethyloxamic, 403.
 ethylsulfonic, 372.
 ethylsulfonic, 360.
 ethylsulfuric, 349, 359, 372, 423, 424.
 euxanthic, 732.
 fellic, 635.
 ferric, 199.
 fluorenic, 496.
 formic, 287, 297, 308, 328, 329, 341, 345, 427, 428, 533.
 formylacetic, 362.
 fulminic, 396.
 fulminuric, 396.
 fumaric, 344, 430, 431, 601.
 furfuran carboxylic, 510.
 gadinic, 367.
 galactonic, 315.
 gallic, 450, 461.

- Acid, gallotannic, 461.
 gentisinic, 460.
 gluconic, 314, 315, **343**.
 glucosamic, 420.
 glucovanillic, 466.
 glucuronic, 326, 346, **348**, 509, 541, 684, 732.
 glutaconic, 431.
 glutamic, **419**, 580, 617, 629, 763.
 glutaminic (see Glutamic).
 glutaric, 334, **337**, 552.
 glyceric, 297, 331, **342**, 417, 420.
 glycerophosphoric, **365**, 644.
 glycocholic, 413, 421, **636**.
 glycolamic, 413.
 glycollic, 295, 297, 301, 330, 339, **341**, 413.
 glycoluric, 407, 515.
 glycosuric, 461, 743.
 glyoxylic, 269, 297, 330, **346**, 515, 713.
 graphitic, 188.
 guanidinbutyric, 418.
 guanylic, 592.
 guanylnucleic, 534.
 hæmatinic, 510, 664.
 Acid halids, aliphatic, 352.
 aromatic, 468.
 Acid, heptylic, 333.
 hexahydro-tetroxybenzoic, 492.
 hippuric, 413, 414, 456, **479**, 528, 606, 640, 720, 724, 756.
 homogentisinic, 461.
 homoprotocatechuic, 461.
 hydantoic, 406, **407**, 515.
 hydraacrylic, 331, **342**.
 hydrazoic, 152.
 hydrindic, 541.
 hydriodic, 136.
 hydrobromic, 134.
 hydrochlorauric, 193.
 hydrochloric, 130, 609.
 hydrochloroplatinic, 214.
 hydrocinnamic, 458.
 hydrocyanic, 300, 329, **391**, 398, 401, **410**, 413, 420, 425, 454, 466, 530, 537.
 hydrofluoric, 126.
 hydrofluosilicic, 191.
 hydronitroprussic, 399.
 hydroparacoumaric, 460.
 hydroplatinocyanic, 399.
 hydroquinone carboxylic, 460.
 hydrosulfuric, 139.
 hydrosulfurous, 144.
 hypobromous, 135.
 hypochlorous, 133.
 hypogæic, 429.
 hyponitric, 155.
 hyponitrous, 156.
 hypophosphoric, 166, **168**.
 hypophosphorous, 166.
 hyposulfurous, 143, **144**, 147.
 hypoxanthylic, 592.
 ichthulinic, 586.
 indigodisulfonic, 542.
 indigomonosulfonic, 542.
 indoleacetic, 540.
 indoleamidopropionic, 540.
 indoxylglucuronic, 729.
 indoxylie, 541.
 indoxylsulfuric, 541, 728.
 iodic, 137.
 iodopropionic, 331, 428.
 isatoic, 542.
 isatropic, 553.
 isethionic, 372, 421.
 isobarbituric, 529.
 isobutylformic, 332.
 isobutyric, 332.
 isocrotonic, 429.
 isocyanic, 396, 408.
 isodialuric, 529.
 isonicotinic, 519, 545.
 isophthalic, 457.
 isopropylacetic, 332.
 isopropylbenzoic, 456.
 isopropylformic, 332.
 isosaccharic, 510.
 isostrychnic, 560.
 isosuccinic, 334, **337**.
 isothiocyanic, 397.
 isovaleric, 332.
 isovanillic, 460.
 itaconic, 346, 431.
 kynurenic, 544.
 kynuric, 541, **544**.
 lactic, 331, **341**, 428, 601, 620, 623, 684, 721, 761.
 lævolactic, 342.
 lævotartaric, 314, 344, **345**.
 lævulinic, **347**, 593.
 lauric, 333.
 laurostearic, 333.
 leucic, 342.
 linoleic, 429, **430**.
 lithic, 528.
 lithofellic, 649.
 lysuric, 419, **480**.
 maleic, **430**, 601.
 malic, 337, **344**, 345, 419, 431, 467.
 malonamic, 403.
 malonic, **337**, 526, 529.
 maltonic, 343.
 mandelic, 463.
 mannonic, 298.
 mannosaccharic, 298.
 margaric, 333.
 meconic, 517.
 meconinic, 462.
 mesaconic, 431.
 mesotartaric, 314, 344, **345**, 430.
 mesoxalic, 269, **347**.
 metaboric, 187.
 metahemipinic, 565.
 metanitrous, 156.
 metantimonous, 185.
 metaphosphoric, 166, **168**.
 metaphosphorous, 166.
 metarsenic, 173, **178**.
 metarsenous, 173.
 metastannic, 212.
 metatungstic, 192.
 methacrylic, 429.
 methylacetic, 330.
 methylacrylic, 524.
 methylecrotonic, 429.
 methylenesuccinic, 431.
 methylethylacetic, 332.
 methylfumaric, 431.
 methylguanidinaetic, 389.
 methylmaleic, 431.
 methylmalonic, 337.
 methylphenolsulfonic, 464.
 methylsuccinic, 334, 338.
 monobromopropionic, 428.
 monobromosuccinic, 431.

- Acid, monochloroacetic, **330**, 337, 384, 412, 414, 479, 528, 529.
 morintannic, 462.
 morphinsulfuric, 563.
 morphylsulfuric, 563, 673.
 morrhucic, 571.
 mucic, 346, 510.
 muriatic, 130.
 myristic, 333.
 myronic, 467.
 naphthalenesulfonic, 498, 516.
 naphthalic, 500.
 nicotinic, **519**, 545, 551, 556.
 nitric, 157.
 nitroacetic, 410.
 nitrocinnaamic, 539, 542.
 nitrohydrochloric, 131.
 nitrophenylacetic, 541.
 nitrosomalonic, 419.
 nitrosulfonic, 155.
 nitrotoluenesulfonic, 480.
 nitrous, 156.
 nonylic, 333.
 octylic, 333.
 oenanthylic, 333.
 oleic, 334, **429**.
 opianic, **463**, 464, 564, 566.
 ornithuric, 418, **480**.
 orsellinic, 461.
 orthoamidobenzoic, 478.
 orthoamidobenzoylformic, 478.
 orthoamidomandelic, 478.
 orthoamidophenylacetic, 478.
 orthoarsenic, 173.
 orthoboric, 187.
 orthocarbonic, 167.
 orthodiazindicarboxylic, 520, **521**.
 orthophenylsulfonic, 470.
 orthophosphoric, 167.
 orthotoluic, 462.
 orthovinylbenzoic, 457.
 orthoxybenzoic, 459.
 orthoxyparatoluic, 460.
 osmic, 192.
 oxalic, 283, 295, 297, 298, 306, 318, 321, 328, 329, 330, 334, **335**, 341, 342, 345, 350, 353, 424, 525, 530, 731.
 oxaluric, **408**, 527, 725.
 oxamic, 401, 463.
 oxanilic, 478, **480**.
 oxyacetic, 341.
 oxyamidopropionic, 420.
 oxybutyric, 342, 753, 756.
 oxycaproic, 342.
 oxyformic, 340.
 oxyglutaric, 337, **344**.
 oxyisobutyric, 339.
 oxymalonic, 344.
 oxymethylbenzoic, 504.
 oxyphenic, 448.
 oxyphenyllactic, 581.
 oxyphenylpropionic, 581.
 oxypropionic, 339, **341**, 347, 428.
 oxyproteic, 730.
 oxyprotosulfonic, 579.
 oxyquinolinecarboxylic, 544.
 oxysalicylic, 449.
 oxysuccinic, 344.
 palmitic, **333**, 429.
 paraamidobenzenesulfonic, 474.
 parabanic, **515**, 530.
 paralactic, 342.
 Acid, paraoxyhydratropic, 467.
 paraoxyphenylacetic, **460**, 647.
 paraoxyphenylglycollic, 460.
 paraoxyphenylpropionic, **460**, 647.
 paraphenylacetic, 460.
 parasorbic, 430.
 paratartaric, 344.
 pelargonic, 333.
 pentathionic, 143.
 pentoxypimelic, 346.
 pepsahydrochloric, 611.
 perbromic, 135.
 perchloric, 133.
 periodic, 137.
 peroxyprotonic, 579.
 persulfuric, 143, **147**.
 phenic, 444.
 phenylacetic, 456, 582.
 phenylacrylic, 525, 553.
 phenylamidopropionic, 478, 580, 582.
 phenylglucuronic, 728.
 phenylglyceric, 463.
 phenylglycollic, 463.
 phenylhydracrylic, 553.
 phenylisocrotonic, 495, 498.
 phenylmalonic, 457.
 phenyloxypropionic, 458.
 phenylpropionic, 458.
 phenylpropionic, 582.
 phenylsulfuric, 470, 728.
 phloretic, 467.
 phocenic, 332.
 phoenicinsulfonic, 542.
 phosphatic, 168.
 phosphocarbonic, 655.
 phosphoglyceric, 365.
 phosphomolybdic, 192, 548.
 phosphoric, 166, 167.
 phosphorous, 166, 167.
 phosphotungstic, 192.
 phthalamic, 464, 477, 478.
 phthalic, 444, **467**, 462, 468, 495, 501.
 phthalidacetic, 464.
 picolonic, 519.
 picric, 459, **472**, 475, 494.
 pimelic, 338, 459.
 piperic, **458**, 550.
 pivalic, 332.
 plumbic, 205.
 propargylic, 430.
 propenylpentacarboxylic, 327, 338.
 propiolic, 430.
 propionic, **330**, 341.
 propylacetic, 332.
 protocatechuic, 460, 461.
 prussic, 391.
 pseudouric, 526, 529.
 purpuric, 527.
 pyrazoledicarboxylic, 512.
 pyridintartronic, 556.
 pyridintricarboxylic, 565, 566.
 pyroantimonic, 185.
 pyroarsenic, 173, 174.
 pyroarsenous, 173.
 pyrobismuthic, 210.
 pyroboric, 187.
 pyrocholesteric, 635.
 pyrogallie, 450.
 pyromucic, 346, 510.
 pyrophosphoric, 166, 168.
 pyrophosphorous, 166.
 pyroracemic, 341, 347, **481**.

- Acid, pyrosulfuric, 143, 147.
 pyrotartaric, 337, 338, 345.
 pyrrolidincarboxylic, 589, 595.
 pyruvic, 347.
 quercitannic, 462.
 quinic, 449, 452, **493**, 556, 559.
 quinolinic, 519.
 quinotannic, 462, 556.
 quinovic, 556.
 racemic, 314, 344, **345**, 430.
 Acid reaction, 62.
 Acid, rheic, 500.
 ricinoleic, 430.
 rocellic, 338.
 rosolic, 444, 450.
 saccharic, 319.
 salicylic, 444, 453, 457, **459**, 468, 478.
 salicylous, 454.
 sebacic, 338, 429.
 silicotungstic, 192.
 skatoleacetic, 581.
 skatolecarboxylic, 540, 581, **646**, 647.
 sorbic, 430.
 sozolic, 470.
 stannic, 212.
 stearic, 333.
 strychnic, 560.
 suberic, 338.
 succinamic, **403**, 408, 419.
 succinic, 287, 331, 334, **337**, **345**, 431, 761.
 sulfanilic, 474, 516.
 sulfhydric, 139.
 sulfindigotic, 542.
 sulfindylic, 542.
 sulfocarbamic, 405.
 sulfocyanic, 396.
 sulfothiocarbonic, 374.
 sulfovinic, 359.
 sulfuric, 143, **144**.
 sulfurous, 142, 143, **144**.
 tartaric, 297, 313, **344**, 347.
 tartronic, 344.
 taurocarbamic, 421, 640, 730.
 taurocholic, 421, **636**, 639.
 terebic, 492.
 terephthalic, 457.
 terpenylic, 492.
 tetraboric, 187.
 tetraoxyamidocaproic, 420, 594.
 tetrathionic, 143.
 thioacetic, 374.
 thioamidopropionic, 421.
 thiobenzoic, 469.
 thiocarbamic, 405.
 thiocarbonic, 396.
 thiocyanic, 373, 396.
 thiolaetic, 374, 580.
 thioxyarsenic, 173.
 thiosulfuric, 143, **147**.
 thymic, 593.
 thymus-nucleic, 524.
 tiglic, 429.
 tricarballic, 327, 338, 431.
 trichloroacetic, 304, **330**, 737.
 trichromic, 195.
 tricyanic, 396.
 trihydrocyanic, 399, 537.
 trimethylacetic, 332.
 trimethyltricarballic, 493.
 trinitrophenic, 472.
 trioxycholesteric, 638.
 trithiocarbonic, 374.
 Acid, trithionic, 143.
 triticonucleic, 593.
 tropic, 457, **463**, 553, 554, 555.
 uric, 403, 405, 413, 414, 515, 522, 524, 527, **528**, 529, 530, 531, 532, 534, 684, 685, 709, 710, 720, 721, 722, 723, 759.
 urochloralic, 732.
 uroferric, 731.
 uroleucic, 461.
 uroproteic, 731.
 urous, 532.
 valerianic, 332.
 vanillic, 454, 460.
 veratric, 449, 460, 565, 569.
 vinylbenzoic, 457.
 xanthic, 532.
 xanthyllic, 592.
 yeast-nucleic, 523, 593.
 Acidism, 754.
 Acidosis, 754.
 Acids, 63, 115, 282, 283 (see Acid).
 acetic series, 327.
 acetylene monocarboxylic, 430.
 alcohol, 338.
 aldehyde, 346.
 ketone, 347.
 alkyl-acetic, 330.
 amic, 379.
 benzoic, 456.
 dithiocarbamic, 397.
 sulfuric, 349.
 amic, 399, 401, 411, 478, 480.
 amido, **411**, 579, 581, 631, **646**, 685, 686, 756.
 butyric, 412, 414.
 caproic, 414.
 cinnamic, 478.
 dicarboxylic, 419.
 glyceric, 420.
 lactic, 420.
 phenyl, 477, 478.
 propionic, 414, 420.
 succinic, 419.
 thio, 421.
 thiolaetic, 421.
 valerianic, 414.
 anil, 481.
 anilic, 480.
 anilido, 478, 479, 480.
 anthracenecarboxylic, 500.
 aromatic alcohol, 462.
 dicarboxylic, 463.
 aldehyde, 464.
 amido, 470, **477**.
 carboxylic, 455.
 dioxyalcohol, 463.
 dioxycarboxylic, 460.
 ketone, 464.
 monocarboxylic, 455.
 nitro, 473.
 polycarboxylic, 456.
 sulfonic, 456, **469**.
 trioxycarboxylic, 461.
 unsaturated, 457.
 azofatty, 380.
 basicity of, 63.
 benzene dicarboxylic, **457**.
 disulfonic, 469.
 sulfonic, 444.
 benzenic, 443.
 benzoic series, 455.
 benzoylbenzoic, 504.

- Acids, benzyl alcohol, 463.**
 biliary, 634, 639, 645.
 bromoacetic, 330.
 bromobenzole, 459.
 bromopropionic, 331.
 camphoric, 492.
 caproic, 332.
 carbopyridic, 517, 519.
 carboxylic, 283, **327**.
 chloroacetic, 330.
 chloropropionic, 331.
 crotonic, 429.
 cyanofatty, 335, **395**, 412.
 diamidobutyric, 417.
 diamidocaproic, 418.
 diamidofatty, **416**, 477.
 diamidovalerianic, 417, 418.
 diatropic, 458.
 dibromofatty, 417.
 dicarboxylic, 328, 362, 395.
 diketone monocarboxylic, 347.
 dimethyluric, 531.
 diolefin monocarboxylic, 430.
 dioxybenzoic, 460, 461.
 dioxydicarboxylic, 344.
 dioxyethylene succinic, 344.
 dioxymonocarboxylic, 342.
 dioxyphenyl, 461.
 dioxytoluic, 461.
 diphenylmethane carboxylic, 504.
 dithiocarbamic, 406.
 fatty, 327, 428.
 fluorene carboxylic, 500.
 gluconic, 314, 315, **343**.
 glyceric series, 342.
 glycocholic, 634.
 guanylic, 593.
 hæmatinic, 510.
 halid fatty, 328, 330, 335, 339, 368, 412.
 hexylic, 332.
 hydroaromatic, 491, 492.
 hydrometalloeyanic, 399.
 hydrophthalic, 457.
 hydroxamic, **388**, 480.
 indigosulfuric, 542.
 iodoacetic, 330.
 iodopropionic, 414.
 isatropic, 458.
 ketonic, 307, **347**.
 lactic, **341**, 414.
 leucic, 415.
 mannonic, 343.
 mannosaccharic, 343, 346.
 mercapturic, 422.
 methylpseudouric, 526, 531.
 methyluric, 531.
 monamido, **411**, 589.
 monamidoxo, 420.
 monocarboxylic, 362.
 aromatic, 455.
 monochlor fatty, 395, 411, 412.
 monohalid fatty, 413, 428.
 monoketone monocarboxylic, 347.
 monoxydicarboxylic, 343.
 naphthalene carboxylic, 500.
 sulfonic, 500.
 naphthoic, 500.
 naphthol carboxylic, 500.
 sulfonic, 498.
 naphthylamin, sulfonic, 501.
 naphthyl fatty, 500.
 nitrilic, 394, 395.
- Acids, nitro, 410, 412.**
 nitrobenzenic, 473, 478.
 nitrocinnamic, 458.
 nitrolic, 376.
 nitropropionic, 414.
 nucleic, 523, 532, 588, 591, **592**.
 nucleinic, 592.
 of antimony, 155.
 arsenic, 173.
 nitrogen, 156.
 phosphorus, 166.
 sulfur, 143.
 olefin dicarboxylic, 335, **430**.
 monocarboxylic, 430.
 tricarboxylic, 431.
 oleic, 428.
 ortho, 167.
 oxalic series, 334.
 oxyacetic, **339**, 428.
 oxyaldehyde, 348.
 oxybenzoic, 459.
 oxybutyric, 340, 342, **413**.
 oxycaproic, 415.
 oxyketone, 348.
 oxymethylbenzoic, 462.
 oxypropionic, 341, 342.
 oxypyrrolidincarboxylic, 579, **580**.
 oxytricarboxylic, 346.
 paraffin dicarboxylic, 334.
 monocarboxylic, 327.
 pentacarboxylic, 338.
 tetracarboxylic, 338.
 tricarboxylic, 338.
 pentoxydicarboxylic, 346.
 pentoxymonocarboxylic, 343.
 phenanthrene carboxylic, 497.
 phenol carboxylic, 458.
 sulfonic, 444, 470.
 phenyl acrylic, 457.
 alcohol, 463.
 alcohol ketone, 464.
 amido, 477.
 diketone, 464.
 phenylene ketone dicarboxylic, 464.
 phenyl fatty, 456.
 hydracrylic, 463.
 ketone, dicarboxylic, 464.
 lactic, 463.
 olefin carboxylic, 457.
 paraffin alcohol, 462, 463.
 propionic, 413, 456, 458.
 phthalic, 457.
 phthalid, 464.
 picolinic, 519.
 polycarboxylic aromatic, 456.
 pure, 327.
 pyridin, carboxylic, 519.
 dicarboxylic, 519, 558.
 pyrrolidincarboxylic, 511, 579, **580**.
 quinolin carboxylic, 558.
 residue of, 63.
 resoreylic, 460.
 saccharic, 346.
 sulfonic, 360, 372, 469.
 sulfobenzoic, 458.
 sulfonic, 360, 370, **372**.
 sulfurous, 144.
 tannic, 461.
 tartaric, 313, **344**.
 taurocholic, 634.
 tetracarboxylic, 338.
 tetroxydicarboxylic, 346.

- Acids, tetroxymonocarboxylic, 343.**
 thio, 370, 374.
 thiocarbamic, 405.
 thiosulfonic, 372.
 thymonucleic, 524, 525, 592, 593.
 toluenesulfonic, 469.
 toluic, 441, 457.
 tricarboxylic, 338.
 trioxycarboxylic, 346.
 trioxymonocarboxylic, 342.
 tropidincarboxylic, 555, 556.
 unsaturated aromatic, 457.
 valerianic, 332, 417.
 volatile fatty, 327.
Acidulous elements, 125.
Acidyl anhydrides, 406.
 chlorids, 300, 351, 393, 398, 400, 406, 446, 504.
 cyanids, 393, 398.
 halids, 300, 307, 328, 352, 359, 401, 410.
 hydroxids, 328.
 oxids, 282.
Acidylens, 334.
Acidyls, 328.
Acipiperazines, 522.
Aconin, 569.
Aconite alkaloids, 568.
Aconitin, 568, 569.
Acridin, 538, 544.
Acrolein, 296, 297, 426, 427, 428.
 acetal, 310.
 bromid, 314.
Acrososazone, 388.
Actinic power, 39.
Actinium, 55, 103.
Acyclic compounds, 271, 273.
Acylation, 369.
Addiment, 672, 675.
Addition, 269.
Adenin, 532, 534, 535, 536, 593.
Adipocere, 582.
Adjacent positions, 437.
Adonite, 298.
Æsculetin, 466.
Æsculin, 466.
Æthiops mineralis, 256.
Affinity, 86.
After-damp, 275.
Agate, 191.
Agglutinins, 670, 672, 675.
Air, 149.
 alveolar, 688.
 ammonium compounds in, 150.
 analysis of, 356.
 carbon dioxide in, 355, 356, 357.
 solid particles in, 150.
Alabaster, 237.
Alanin, 414, 420, 580, 595, 596, 721, 757, 763.
Alanins, 412, 414 (see Acids, amidopropionic).
Alanylalanin, 416.
Albumin, 617.
Albite, 248.
Albumen, 584.
Albuminates, 582, 589, 612.
Albuminoids, 583, 595, 619.
Albumins, 582, 583.
 coagulated, 590.
 coagulating, 582, 585.
 derived, 582, 589.
 native, 582, 583, 589, 590, 591, 624.
Albumins, true, 582, 583.
Albuminuria, 734, 738.
Albumoid, 583, 595.
Albumoses, 582, 612, 628, 646, 736, 737.
 deuterio, 618.
 primary, 613, 616, 624.
 secondary, 613, 615, 616, 618, 625.
Albumosuria, 739.
Alcohol, 287 (see Alcohols).
 absolute, 288.
 acids, 338.
 allyl, 426, 427, 428.
 amidoethyl, 408.
 amylic, 292, 293, 521.
 benzylic, 443, 452.
 bromallylic, 427.
 butylic, 601.
 cetyllic, 294.
 cinnamic, 453.
 coniferyl, 466.
 crotonyl, 427.
 epichlorhydrin, 351.
 ethene, 295.
 ethers, 350.
 ethylic, 287, 400.
 fluorene, 499.
 isobutylic, 601.
 methylic, 288, 300.
 nitroethyllic, 408.
 oxybenzylic, 453.
 propargylic, 426, 427.
 propenyl, 296.
 propylic, 427.
 trichlor, 732.
 vinyl, 426.
Alcoholates, 286, 289, 328, 349.
Alcoholic beverages, 290.
 fermentation, 600.
Alcohols, 284, 302, 379.
 acetylene, 427.
 allyl, 299.
 amido, 408.
 amylic, 292.
 aromatic, 452, 453, 454, 456.
 benzenic, 443.
 butylic, 292.
 camphan, 491.
 diatomic, 282, 284, 294.
 dihydric, 282, 284, 294.
 diolefin, 477.
 diphenyl, 503.
 diprimary, 285, 294.
 heptatomic, 298.
 hexatomic, 284, 298.
 hexahydric, 284, 298.
 hydroaromatic, 489.
 iso, 285.
 menthan, 490.
 menthene, 490.
 monoatomic, 284.
 naphthyl, 499.
 nomenclature of, 284, 285.
 nonatomic, 298.
 octatomic, 298.
 olefin, 426.
 oxyphenyl, 453.
 pentatomic, 284, 297.
 pentahydric, 284, 297.
 polyatomic, 297.
 polyhydric, 297.
 primary, 282, 283, 285, 377.
 propylic, 291.

- Alcohols, ring, 489.**
 secondary, 282, 283, 285, 307, 377.
 ring, 489, 490.
 terpan, 489, 490.
 tertiary, 282, 283, 285, 377, 443.
 tetratomic, 284, 297.
 tetrahydric, 284, 297.
 triatomic, 284, 295.
 trihydric, 284, 295.
 tropan, 552.
- Aldehyde, acetic, 302, 306, 409.**
 acids, 339, 340, 346.
 acrylic, 427.
 alcohols, 299, 308.
 allyl, 428.
 amidobenzoic, 543.
 ammonia, 300, 362, 409, 517, 518.
 anisic, 454.
 benzoic, 443, 453, 457, 458, 463, 466, 468, 503, 504, 505.
 betain, 368.
 butyric, 305, 550.
 cinnamic, 454.
 crotonic, 302, 437.
 cuminic, 447.
 formic, 299, 300, 306, 373, 389, 404, 409, 413, 503, 514.
 furfuric, 509.
 glyceric, 306, 310, 600.
 glycollic, 299, 310, 420.
 green, 506.
 halids, 277.
 hydrates, 306.
 hydrazones, 410.
 isovaleric, 414.
 ketones, 308, 398.
 methylprotocatechuic, 454.
 oxybutyric, 427.
 propargyl, 428.
 propionic, 305.
 salicylic, 453, 454, 468, 539.
 thioformic, 373.
- Aldehydin, 518.**
- Aldehydes, 282, 283, 284, 286, 298, 299, 324, 325, 326, 339, 352, 391, 398, 409, 484, 517, 543, 544.**
 acetylene, 428.
 aromatic, 453, 456.
 benzenic, 443.
 diolefin, 428.
 naphthyl, 499.
 olefin, 427, 428.
- Aldehydrazones, 485.**
- Aldohexoses, 310, 343.**
- Aldol, 300, 308, 420, 427.**
- Aldopentoses, 310.**
- Aldoses, 309, 310, 324, 325, 326, 485.**
- Aldoxims, 379, 398, 409, 410.**
- Ale, 290.**
- Aleurone corpuscles, 587.**
- Alexins, 672.**
- Algaroth, powder of, 184.**
- Aliphatic compounds, 271, 273.**
 unsaturated, 423.
- Alizarin, 495, 499.**
 dyes, 495.
- Alkali, 215.**
 albuminates, 582, 590, 629.
 carbonated, 215.
 caustic, 215.
 metals, 215.
 volatile, 151.
- Alkaline earths, metals of, 235.**
 reaction, 62.
- Alkaloids, 545.**
 aconite, 568.
 atropic, 552.
 cinchona, 556.
 classification of, 548.
 general reactions of, 548.
 isoquinolin, 548, 562.
 opium, 544, 563.
 phenanthrene, 548, 562.
 piperidine, 548, 549.
 piperidin, 548, 549.
 pyridin, 548, 549.
 pyrrolidin, 548.
 piperidin, 548, 552.
 pyridin, 548, 551.
 quinolin, 548, 556.
 separation of, 547.
 strychnos, 559.
 tropan, 552.
- Alkanes, 274.**
- Alkaptonuria, 460, 461, 743.**
- Alkarsin, 422.**
- Alkyl, 294.**
 amide, 401.
 ammonium iodids, 379.
 benzenes, 440.
 cyanidins, 537.
 cyanids, 277, 394.
 halids, 277, 286, 307, 349, 359, 371, 376, 379, 464.
 hydride, 274.
 indoles, 540.
 iodids, 379, 382.
 isocyanids, 394.
 mercaptopyrimidins, 534.
 pseudothiouras, 523.
 pyridins, 518.
 pyridinum iodids, 518.
 thiopseudouras, 406.
 ureas, 402, 406.
- Alkylation, 370.**
- Alkylen dicyanids, 395.**
 oxids, 350, 382.
- Alkylens, 294, 350.**
- Allantoin, 515, 527, 530, 713, 725.**
- Allene, 425.**
- Allometa position, 438.**
- Allortho position, 438.**
- Allotropy, 17.**
- Alloxan, 348, 403, 515, 526, 527, 530.**
- Alloxantin, 526, 527, 530.**
- Alloxuric bases, 531.**
- Allyl alcohol, 299.**
 amin, 432.
 anilin, 543.
 bromid, 432, 552.
 cyanids, 428.
 guaiacol, 450.
 halids, 426, 428.
 iodid, 426, 431, 432.
 isothiocyanate, 397, 432, 467.
 oxid, 431.
 phenol, 450.
 pyrocatechol, 450.
 sulfid, 432.
 tetraoxvbenzene, 450.
 tribromid, 296.
- Allylene, 425, 442.**
- Alphenols, 453.**
- Alumina, 246.**

- Aluminates**, 245, 246, 247.
Aluminium, 245.
 chlorid, 247, 441, 455, 464, 477, 495, 499, 501, 502, 504.
 group, 245.
 hydroxid, 246.
 oxid, 246.
 silicates, 248.
 sulfates, 247.
Alums, 247.
Amalgams, 255.
Amanitin, 383, 385.
Amber, 337, 493.
Ambergris, 649.
Amboceptor, 672, 675.
Ambralin, 649.
Amid, amidoglutaric, 420.
 benzoyl, 477.
 glycocoll, 407.
 sarcosin, 407.
 ethylene-ethenyl, 385.
Amidins, 388.
Amido acetaldehyde, 409, 521.
 acetones, 409.
 acids, 411.
 aromatic, 477.
 alcohols, 408.
 aldehydes, 409.
 azo compounds, 483.
 benzenes, 471, 473, 501.
 cyanidins, 537.
 diphenyls, 502.
 group, 380, 413.
 guanidin, 389.
 ketones, 409.
 ketopurin, 534.
 malononitril, 391, 395, 537.
 malonylurea, 526, 529.
 naphthalenes, 500.
 paraffins, 376, 377.
 phenyl acids, 478.
 phenols, 448, 473, 477.
 purin, 535.
 thioacids, 421.
 toluyls, 502.
 triphenyl carbinols, 506.
 methanes, 505.
 uracil, 529.
 xylenes, 474.
Amidoxims, 388, 481.
Amids, 328, 379, 388, 395, 399, 407 (see Monamids, Diamids).
 amidossuccinic, 419.
 aromatic, 470, 477.
 mixed, 399, 401.
 of dicarboxylic acids, 401.
 primary, 399.
 secondary, 399.
 tertiary, 399.
Amin, allyl, 432.
 bases, 377.
 nitrosodimethyl, 380.
 trimethyltrimethylene, 380.
 vinyl, 432.
Amins, 286, 301, 377, 381, 397, 401, 406, 410, 413, 581 (see Monamins, Diamins).
 aromatic, 302, 470.
 cyclic, 380.
 mixed, 377.
 naphthyl, 499, 500.
 nitroso, 380.
 primary, 380, 394, 397, 482.
 secondary, 302, 482.
 simple, 377.
 unsaturated, 382.
Ammelid, 404, 537.
Ammelin, 537.
Ammeter, 45.
Ammonia, 151.
 caustic, 232.
Ammonias, compound, 377.
Ammonio-magnesian phosphate, 241, 705.
Ammonium, 151, 232.
 acetate, 234.
 amalgam, 232.
 bromid, 233.
 butyrate, 332.
 carbamate, 402, 403, 681, 685, 686, 712.
 carbonates, 234, 402, 685, 712.
 chlorid, 233.
 cyanate, 262.
 derivatives, 377.
 hydroxid, 232.
 iodid, 233.
 isocyanate, 403.
 isothiocyanate, 406.
 nitrate, 233.
 nitrite, 380.
 sesquicarbonate, 234.
 sulfamate, 232.
 sulfates, 233, 234, 576.
 sulfhydrate, 233.
 sulfids, 233.
 theory, 232.
 urates, 531, 720, 723, 759.
Ampère, 44.
Amphocreatinin, 390.
Amphopeptone, 616.
Amphoteric elements, 101, 193.
Amygdalin, 391, 453, 466.
Amyl acetate, 363.
 caprate, 333.
 chlorid, 293.
 cyanid, 332.
 nitrate, 362.
 nitrite, 363.
Amylamin, 415.
Amylase, 605, 654.
Amylene, 294, 425.
 hydrate, 294.
Amylodextrin, 643.
Amyloid, 583, 597.
Amylopsin, 627, 631.
Amylum, 320.
Anachlorhydria, 619, 643.
Analysis, 62, 115, 599.
 organic, 265.
Analytical characters of alcohol, 289.
 aluminium, 248.
 ammonium, 234.
 anilin, 474.
 antimony, 181, 186.
 arsenic, 178.
 atropin, 554.
 barium, 239.
 bismuth, 210.
 bromidion, 134.
 brucin, 561.
 cadmium, 245.
 calcium, 238.
 carbolic acid, 445.
 chloridion, 132.
 chloroform, 279.
 chromium, 196.

Analytical, cobalt, 249.

cocain, 556.
 conifin, 550.
 copper, 253.
 cyanids, 392.
 gold, 194.
 hydrogen, 108.
 sulfid, 141.
 iodidion, 137.
 iron, 203.
 lead, 207.
 lithium, 216.
 magnesium, 372.
 manganese, 196.
 mercury, 260.
 morphin, 563.
 nickel, 249.
 nicotin, 651.
 nitrates, 158.
 oxalates, 336.
 oxygen, 112.
 ozone, 112.
 phenol, 445.
 phosphates, 168.
 phosphorus, 163.
 potassium, 239.
 quinin, 557.
 silver, 231.
 sodium, 231.
 strontium, 238.
 strychnin, 560.
 sulfates, 146.
 sulfids, 141.
 sulfur dioxid, 143.
 tin, 213.
 zinc, 244.

Anethol, 450, 454.**Anglesite, 204.****Anhydrid, acetic, 351, 369, 406, 496, 539.**

antimonic, 184.
 antimonous, 184.
 arsenic, 172.
 arsenous, 172.
 benzoic, 468, 480.
 boric, 187.
 carbonic, 354.
 chromic, 195.
 citraconic, 431.
 glycocoll, 412, 416, 522.
 itaconic, 431.
 leucin, 522, 630.
 maleic, 344, 419, 430.
 manganic, 196.
 manganous, 196.
 molybdic, 192.
 nitric, 156.
 nitrous, 154.
 phosphoric, 166.
 phosphorous, 166.
 phthalic, 449, 450, 451, 462, 468, 477.
 plumbic, 205.
 silicic, 191.
 succinic, 337.
 sulfuric, 143.
 sulfurous, 142.
 titanic, 211.
 tungstic, 192.

Anhydrids, 84, 111, 282, 286, 300, 328, 335, 351.

aromatic, 468.
 benzenic, 443.
 cyclic, 412.

Anhydrids, mixed, 352.

 of monamido acids, 522.
 thio, 141, 374.

Anhydroecgonin, 555.**Anhydrogeraniol, 426.****Anilido acids, 479.****Anilids, 476, 480.**

 of dicarboxylic acids, 478.

Anilin, 471, 473, 475, 476, 479, 481, 482, 483, 484, 505, 509, 522, 540, 542.

 derivatives of, 475.

 dyes, 476, 481, 483, 505.

 red, 506.

Anilins, 543.**Anils, 452.****Animal gum, 654.****Anions, 44, 72.****Anisidins, 472, 477.****Anisol, 464.****Annidalin, 448.****Anode, 41.****Anol, 450.****Anthracene, 493, 495, 497.**

 halids, 497.

 nitrogen derivatives of, 500.

 oil, 440.

Anthracite, 188.**Anthranol, 499.****Anthraphenols, 498.****Anthrapyridins, 538.****Anthraquinolins, 538.****Anthraquinone, 495, 496, 499.****Anthrols, 499.****Antialbumid, 613, 618, 629.****Antifebrin, 476, 513.****Anti bodies, 670.****Anti group, 612, 618.****Antihæmolytins, 672.****Antimony, 148, 183.**

 acids of, 185.

 antimonate, 185.

 black, 185.

 butter of, 184.

 chlorids of, 183.

 cinnabar, 186.

 crocus of, 185.

 glass of, 185.

 intermediate oxid of, 185.

 liver of, 185.

 organic compounds of, 422.

 oxids of, 184.

 oxychlorid, 184.

 oxysulfids, 186.

 pentachlorid, 184.

 pentasulfid, 186.

 pentoxid, 184.

 sulfids of, 185.

 tartarated, 227.

 trichlorid, 183.

 trioxid, 184.

 trisulfid, 185.

 vermillion, 186.

Antimonyl, 227.**Antipeptones, 629.****Antipyrin, 484, 512, 513.**

 salicylate, 514.

Antitoxins, 669, 670, 673, 674.**Antitussin, 502.****Apiol, 450.****Apo alkaloids, 547.****Apostropin, 554.****Apomorphin, 562, 565.**

- Apoquinin, 558.
 Aqua ammoniac, 151.
 fortis, 157.
 regia, 131, 158.
 sapphirina, 252.
 Arabin, 321.
 Arabinose, **310**, 321.
 Arbacion, 588.
 Archil, 449.
 Arecaidin, 548, 549.
 Arecaïn, 548, 549.
 Arecolin, 548, 549.
 Arginin, 403, 417, **418**, 480, 580, 581, 586,
 589, 595, 617, 629, 632, 757, 763.
 Argol, 226.
 Argon, 55, 101, 103, 125.
 Aricin, 556.
 Aristol, 447.
 Aromatic compounds, 272, **435**, 439.
 Arragonite, 237.
 Arsenamin, 170.
 Arsenic, 148, **169**, 172, 175.
 disulfid, 174.
 organic compounds of, 422.
 pentasulfid, 174.
 pentoxid, 172.
 tribromid, 171.
 trichlorid, 171.
 trifluorid, 171.
 triiodid, 171.
 trioxid, 172, 175.
 trisulfid, 174.
 Arsenites, 172.
 Arsin, dimethyl, 422.
 Arsinia, 170.
 Arsins, 422.
 Arterin, 659.
 Artiaids, 59.
 Asbestos, 240.
 Asellin, 367.
 Aseptol, 470.
 Asparagina, 403, **419**.
 Aspergillus, 601, 602.
 Asymmetric carbon atom, 312, 313.
 Atmosphere, 149, 355.
 ammoniacal compounds in, 150.
 carbon dioxid in, 150, **355**.
 nitrous acid in, 150.
 solid particles in, 150.
 sulfurous acid in, 150.
 water in, 150.
 Atom, 53.
 Atomic heat, 55.
 rearrangement, 62.
 theory, 52.
 weight, 54.
 Atomicity, 59, 339.
 Atropamin, 554.
 Atropin, 463, 548, 552, **553**.
 Auric chlorid, 193.
 Aurin, 450.
 Auroamidoimid, 396.
 Aurous chlorid, 193.
 Autodigestion, 630.
 Autolysis, 628, 629, **630**.
 Avogadro, postulate of, 52.
 Azins, 520.
 Azobenzene, **483**, 484, 502.
 Azo compounds, 380, 470, 481, **488**, 498.
 Azolimid, 152.
 Azoles, 511.
 Azonaphthol compounds, 498.
 Azoxy compounds, 482, 483.
 Azurite, 252.
 Bacillus acidi laevolactici, 342.
 Bacteria, 581.
 Bacterial fermentations, 601.
 Bacterium aceti, 329.
 Bacteriolysins, 671.
 Baking powders, 227.
 Balsams, 493.
 Barium, 235, 239.
 carbonate, 239.
 chlorid, 239.
 cobaltite, 249.
 dioxid, 239.
 hydroxid, 239.
 monoxid, 239.
 nitrate, 239.
 oxids, 239.
 peroxid, 239.
 pyromucate, 509.
 sulfate, 239.
 Baryta, 239.
 Bases, 63, 64.
 acidity of, 64.
 atomicity of, 64.
 Bassorin, 321.
 Basyous elements, 102, **215**.
 Battery, galvanic, 41.
 Beauxite, 245, 247.
 Beer, 290.
 Beeswax, 363.
 Belladonnin, 553, 555.
 Benzamid, 456, **477**, 479, 480.
 Benzene, 425, 433, **435**, 440, 444, 471, 477,
 484, 495, 501, 502, 504, 510.
 amido, 473.
 amido derivatives of, 470, 471, **473**.
 azomethane, 483.
 carboxylic acids, 414.
 halids, 441, 442.
 hexagon, 435.
 homologues of, 440.
 hydroxylamin derivatives of, 470, 471,
 473.
 imido derivatives of, 470.
 nitro, 471.
 nitro derivatives of, 470.
 nitrogen derivatives of, 470, 471.
 nitroso derivatives of, 470, **473**.
 sulfochlorid, 380, 469.
 Benzenyl, 456.
 amidin, 456.
 amidoxim, 481.
 Benzhydrol, 503, 504, 505.
 Benzidin, 484, **502**.
 Benzil, 504.
 Buzine, 276.
 Benzodiazins, 521.
 Benzofurfurane, 539.
 Benzoin, 504.
 Benzol, 440.
 Benzolene, 276.
 Benzometadiazins, 521.
 Benzonitril, 476.
 Benzoparadiazins, 521.
 Benzophenol, 444.
 Benzophenone, 503, 504.
 Benzopyridin, 538.
 bases, 543.
 Benzopyrones, 539.
 Benzopyrrole, 538, 539.

- Benzoquinone**, 452.
Benzorhodiazins, 521.
Benzosol, 448.
Benzoyl, 443, 456, 478.
 amid, 477.
 chlorid, 298, 311, 323, 324, 369, 385, 417, 454, 455, 468, 477, 479, 480, 537.
 cyanid, 454, 468.
 diazolimid, 152.
 ecgonin, 548, 552, 555.
 glycocoll, 479.
 hydrid, 458.
 ornithin, 480.
 salicin, 468.
 sulfonic imid, 470.
Benzyl, 443.
 acetate, 468.
 benzene, 439, 503.
 chlorid, 443, 502.
 hydrate, 452.
 sulfid, 503.
Berberin, 548.
Beryl, 245.
Beryllium, 245.
Betaïn, 384, 385.
 aldehyde, 384, 385.
 chlorid, 384.
 hydrochlorid, 385.
 methylnicotin, 549.
 trimethylacetic, 384.
Betaïns, 384.
Beverages, alcoholic, 290.
Besoar stone, 649.
Bidiphenyleneethane, 494.
Bieberich scarlet, 498.
Biliary pigments, 634, 637, 640, 641, 642.
 salts, 634, 639.
Bilicyanin, 637.
Bile, 633, 645, 678, 680.
 acids of, 635, 636.
 bilirubin in, 637.
 billiverdin in, 638.
 bladder, 634, 637.
 cholesterol in, 638, 639, 642.
 composition of, 634.
 coloring matters of, 634, 637, 640, 641, 642.
 function of, 633.
 hepatic, 634, 637.
 iron in, 641.
 lecithins in, 635.
 quantity of, 634.
 salts of, 635, 640.
 sodium glycocholate in, 636.
 sodium taurocholate in, 636.
 urea in, 635.
Bilifuscin, 638.
Bililumin, 638.
Billineurin, 383.
Billiprasin, 638.
Bilirubin, 604, 636, 640, 641.
Billiverdin, 636, 637.
Bismark brown, 476.
Bismuth, 148, 209.
 hydroxid, 209.
 nitrate, 210.
 oxids of, 209.
 pentoxid, 210.
 subcarbonate, 210.
 subnitrate, 210.
 sulfid, 210.
 trichlorid, 210.
Bismuth trioxid, 209.
Bismuthates, 209.
Bismuthyl, 209.
 carbonate, 210.
 chlorid, 210.
 hydroxid, 210.
 nitrate, 210.
Biuret, 404, 407, 525.
Bleaching powder, 236.
Blends, 242.
Blood, 649, 667.
 alkalinity of, 667, 676.
 arterin in, 659.
 carbohydrates in, 654, 681.
 carbon dioxid in, 690.
 changes in, 677.
 chemical examination of, 675.
 clot, 649, 667.
 coagulation of, 649, 667.
 coloring substances, 659.
 corpuscles, 649, 656.
 composition of, 658.
 stroma of, 658.
 electrical conductivity of, 658, 676.
 freezing point of, 658, 676.
 gases of, 688.
 laking of, 656.
 osmotic pressure of, 658.
 plasma, 649.
 reaction of, 667, 676.
 serum, 649, 650, 653.
 and bacterial action, 669.
 specific gravity of, 675.
Blue stone, 251.
Boas' process, 623.
Bog ore, 202.
Boiling, 29, 32.
 point, 22, 32.
 absolute, 30.
 elevation of, 31, 32, 68, 69.
Bone ash, 237.
 black, 189.
 oil, 517, 543.
Borax, 187, 219.
Bordeaux dyes, 498.
Borneo camphor, 488, 491.
Borneol, 491, 492.
Boroglycerid, 187.
Boron, 187.
 trioxid, 187.
Böttcher's crystals, 387.
Braunite, 195.
British gum, 321.
Bromacetophenone, 400, 541.
Bromal, 305.
 hydrate, 305.
Bromanilins, 475.
Bromidion, 134.
Bromids, 134.
Bromin, 125, 133.
Bromindene, 496.
Bromoform, 297.
Bromol, 448.
Bromophenols, 448.
Brucin, 559, 561.
Butalanin, 414.
Butaldehyde, 305.
Butandiol, 305.
Butane, 273.
Butene, 273.
Butone, 273.
Butter, 763.

- Butter**, adulterations of, 762, 763.
 fat, 712.
Cacodyl, 422.
 cyanid, 423.
 oxid, 422.
Cadaverin, 386, 418, 581, 617, 758.
Cadet, liquid of, 422.
Cadmium, 240, 245.
Caffein, 528, 532, 533, 546.
Calamine, 242, 244.
Calcepar, 237.
Calcium, 235.
 acetylid, 425.
 carbide, 236, 424.
 carbonate, 237.
 chlorid, 236.
 formate, 300.
 group, 235.
 hydroxid, 236.
 hypochlorite, 236.
 oxalate, 238.
 oxid, 235.
 paracasein, 617.
 phosphates, 237.
 plumbite, 205.
 salts, 668, 745.
 sulfate, 237.
 superphosphate, 237.
 urate, 531.
Calculi, ammonio-magnesian, 705.
 analysis of, 760.
 biliary, 636, 638, 643.
 cystin, 759.
 fusible, 705, 759.
 intestinal, 649.
 mulberry, 238, 731, 759.
 oxalate, 759.
 phosphatic, 705, 759.
 salivary, 608.
 urate, 759.
 uric acid, 759.
 urinary, 697, 705, 756.
 xanthin, 759.
Calomel, 256.
Calorie, 22.
Camphans, 487, 488.
Camphene, 488, 491, 492.
Camphol, 491.
Camphor, 492.
 artificial, 488.
 Borneo, 488, 491.
 Japan, 492.
 laurel, 492.
 momobromo, 492.
Camphors, 487.
Campobello, yellow, 498.
Cane sugar, 316.
Caramel, 317.
Carbamid, 402, 403.
Carbamins, 394.
Carbamyl chlorid, 402.
Carbanil, orthoxy, 475.
Carbazole, 501, 538, 543.
Carbids, 425.
Carbimid, 396, 402, 408.
Carbinamins, 382.
Carbinol, 285, 286.
 butyl, 293.
 diethyl, 293.
 diphenyl, 503, 504.
 diphenyltolnyl, 503.
 Carbinol, sethyl, 291.
 ethylidimethyl, 294.
 ethylmethyl, 292.
 isobutyl, 293.
 isopropyl, 292.
 methyl, 287.
 methylisopropyl, 294.
 methylpropyl, 293.
 phenylidimethyl, 453.
 phenylmethyl, 453.
 propyl, 292.
 trimethyl, 292.
 triphenyl, 503, 504.
Carbocyclic compounds, 272, 433, 434.
Carbodiimids, 474.
Carbohydrates, 309, 509, 642, 643.
 of blood serum, 654.
 tests for, 323.
Carbolates, 446.
Carbolic oil, 440.
Carbon, 188.
 compounds of 262.
 dichlorid, 280.
 dioxid, 353, 354, 690.
 hæmoglobin, 663.
 disulfid, 275, 373, 374, 380, 397.
 group 188.
 metallic, 189.
 monoxid, 275, 352.
 hæmoglobin, 354, 662.
 oxids of, 352.
 oxysulfid, 375, 397.
 tetrabromid, 280.
 tetrachlorid, 275, 380, 458.
 trichlorid, 280, 281, 364.
Carbonic oxid, 352.
Carbonous oxid, 352.
Carbonyl, 270, 299.
 chlorid, 353, 402, 403, 407, 408, 504.
 diurea, 406, 408.
Carborundum, 191.
Carbostyryl, 544.
Carbotriamin, 388.
Carboxim, 409, 410.
Carboxyl, 270, 383, 328, 370.
Carbylamins, 380, 394.
Carbyloxim, 396.
Carnallite, 222.
Carnin, 532, 536, 724.
Carvacrol, 447, 491, 492.
Carvol, 447, 491.
Carvone, 491.
Carvoxims, 492.
Casein, 582, 586, 617, 633, 763.
Caseinogen, 764.
Caseinosea, 613.
Cassel yellow, 206.
Cassiterite, 212.
Catalysers, 108.
Catechol, 729.
Cathode, 41.
Cations, 44, 72.
Celestine, 238.
Cell globulins, 582, 653, 666.
Cellulin, 322.
Cellulase, 605.
Celluloid, 323.
Cellulose, 322, 643.
 nitro, 323.
 starch, 321.
Celsius' scale, 22.
Centigrad scale, 22.

- Cerebrin, 315, 586.
 Cerebrose, 315.
 Cerium, 55, 102, 103.
 Ceruse, 207.
 Ceryl cerotate, 363.
 hydroxid, 294.
 Cesium, 215.
 Cetin, 363.
 Cetyl hydroxid, 294.
 palmitate, 363.
 C. G. S. system, 7.
 Chalk, 235, 237.
 precipitated, 238.
 Characterising groups, 270.
 Charcoal, 189.
 animal, 189.
 Charcot's crystals, 387.
 Chavicol, 450.
 Chemical activity, 75.
 affinity, 86.
 energy, 86.
 equilibrium, 87.
 force, 86.
 terms, orthography of, 771.
 Chemism, 86.
 Chemistry, 2.
 general, 1.
 inorganic, 107.
 mineral, 107.
 organic, 262.
 physical, 3.
 physiological, 574.
 Chinovose, 311.
 Chitin, 387, 597.
 Chitosamin, 387.
 Chitose, 388.
 Chloracetone, 540.
 Chloracetyl alanin, 416.
 glycin, 416.
 glycylglycin, 416.
 Chloral, 303, 330.
 alcoholate, 303, 304.
 butyric, 306.
 hydrate, 269, 278, 304, 401.
 Chloralamid, 401.
 Chloralid, 304.
 Chloralimid, 401.
 Chloralum, 247.
 Chloranilins, 447, 475.
 Chloraurates, 193, 381.
 Chlorhydrargyrate, 255, 258.
 Chloride of lime, 236.
 Chloridion, 77, 132.
 Chlorids, 131.
 Chlorin, 125, 127, 133.
 group, 125.
 monoxid, 133.
 peroxid, 133.
 tetroxid, 133.
 Chlorindones, 496.
 Chlorobenzenes, 437, 442.
 Chlorobromobenzenes, 438.
 Chlorocarbon, 280.
 Chloroform, 278, 304, 380, 391, 394, 401,
 424, 476, 502.
 Chloromercurates, 255, 258.
 Chloromethyl, 278.
 Chlorophenols, 447.
 Chlorophyll, 301, 598.
 Chloroplatinates, 214, 381.
 Chloropurins, 532, 534.
 Chlorozone, 220.
 Cholesterol, 584, 586, 624, 638, 639, 642, 654,
 666, 680.
 Choletelin, 637.
 Cholin, 367, 388, 385, 386, 581, 644.
 Chondroitin, 594.
 Chondromucoid, 594.
 Chondrosin, 594.
 Chromates, 195.
 Chrome yellow, 206.
 Chromium, 194.
 green, 195.
 oxids of, 194.
 Chrysarobin, 500.
 Chrysazol, 499.
 Chrysene, 493, 494, 496.
 Chyle, 692, 693.
 Chyluria, 642.
 Chyme, 619, 628, 645.
 Chymosin, 617.
 Chymosinogen, 617.
 Cider, 291.
 Cinchona alkaloids, 547, 556, 558.
 red, 556.
 Cinchonidin, 519, 556, 558.
 Cinchonin, 519, 543, 556, 558, 559.
 Cinene, 487.
 Cineol, 487, 490.
 Cinnabar, 254.
 Cinnamene, 442, 495.
 Cinnamyl cocaïn, 545, 552.
 Circuit, electric, 40.
 Cisterpin, 490.
 Citronellal, 428.
 Classification of alkaloids, 548.
 of aromatic compounds, 439.
 of carbocyclic compounds, 434, 439.
 of heterocyclic compounds, 507, 508.
 of organic compounds, 271.
 of proteins, 582.
 Clay, 245, 248.
 ironstone, 202.
 Closed chain compounds, 433.
 Clot, 649.
 Clupein, 589.
 Coagulated albumins, 583.
 Coagulating albumins, 582, 585.
 Coagulation, 575, 667.
 temperature, 576.
 Coal, 188.
 tar, 440.
 Cobalt, 249.
 Cobaltcyanids, 399.
 Cocaïn, 548, 552, 555.
 Codein, 562, 564, 565, 566, 567.
 Coefficient, isotonic, 657.
 of distribution, 28.
 Cœrulignone, 502.
 Cohesion, 13.
 Coke, 189.
 Colchicin, 569.
 Colcothar, 198.
 Collagen, 583, 596, 619.
 Collidins, 518.
 Colloids, 18, 575.
 Colophany, 488.
 Columbium, 55, 101, 103.
 Combinations, 62.
 Combustion, 111.
 supporters of, 111.
 Complement, 672, 675.
 Components, 96.
 Composition, 84.

- Compound ammonias, 377.
 Compounds, 47, 48, 54.
 Compounds, acyclic, 271, 273.
 aliphatic, 271, 273.
 aromatic, 272, 439.
 carbocyclic, 272, 433, 434.
 closed chain, 272, 433.
 cyclic, 272, 433.
 fatty, 271, 373.
 heptacarboyclic, 434.
 heterocyclic, 272, 433.
 hexacarboyclic, 434, 435.
 monobenzenic, 439, 440.
 open chain, 271.
 organic, 262, 271.
 pentacarboyclic, 434.
 saturated, 268, 273.
 tetracarboyclic, 434.
 tricarboyclic, 434.
 unsaturated, 269.
 Conchiolin, 597.
 Concentration, 2, 18, 64.
 Condensation, 21, 32, 301, 302, 361.
 Condensed carbocyclic compounds, 493.
 heterocyclic compounds, 537.
 nuclei, 493.
 Condensing agents, 301.
 Conductance, 45.
 Conductivity, equivalent, 74.
 molecular, 74.
 Conductors, 39.
 Congelation, 28.
 Conglutin, 584.
 Congo red, 502.
 yellow, 502.
 Conhydrin, 548, 549.
 Coniferin, 454.
 Conicein, 548.
 Conifin, 414, 518, 519, 548, 549.
 Conjugate glucuronates, 684, 750.
 Consecutive positions, 437.
 Constitution, 84, 264, 268.
 Contact action, 349.
 agent, 108.
 Conyryn, 518.
 Copper, 250, 634.
 acetates, 252.
 acetylid, 423, 425.
 ammonio-sulfate, 252.
 carbonates, 252.
 chlorids, 251.
 glycolamate, 414.
 group, 250.
 hydroxids, 251.
 oxids, 250.
 sulfids, 251.
 Copperas, 200.
 Coprolites, 237.
 Corallin, 444, 450.
 Coridins, 519.
 Corrosive sublimate, 257.
 Corrosives, 132.
 Corundum, 246.
 Cosmolin, 277.
 Cotarnin, 564, 566.
 Coulomb, 44.
 Coumarin, 466, 539.
 Coumarins, 539.
 Coumarone, 539.
 Cream, 762.
 Creamometer, 762.
 Creasol, 446.
 Creosote, 446.
 oil, 440.
 Creatin, 389, 403, 414, 719, 720.
 Creatinin, 389, 390, 709, 710, 712, 718.
 Creolin, 446.
 Cresol, 444, 581.
 Cresols, 446.
 Cresylols, 446.
 Cristallin, 473.
 Croton, 573.
 Croton chloral hydrate, 306.
 Crusocreatinin, 390.
 Cryolyte, 126, 220, 245.
 Crystal violet, 506.
 Crystallization, 13.
 Crystalloids, 18.
 Cupric acetate, 252.
 arsenite, 252.
 carbonate, 252.
 chlorid, 251.
 hydroxid, 251.
 nitrate, 251.
 oxid, 250.
 sulfate, 251.
 sulfid, 251.
 Cuprous chlorid, 251.
 oxid, 250.
 sulfid, 251.
 Curarin, 561.
 Curd, 617.
 Current density, 43.
 normal, 45.
 divided, 43.
 strength, 41, 44.
 Curtius' base, 416, 630.
 Guzeohygrin, 548.
 Cyamelid, 396, 402.
 Cyanacetamid, 395.
 Cyanamid, 388, 389, 398, 406, 414, 418, 421.
 Cyanamids, substituted, 398.
 Cyanhydrins, 391, 397.
 Cyanic esters, 328.
 Cyanidin, 536, 537.
 Cyanids, 391, 393.
 alkyl, 277.
 compound, 398.
 double, 398.
 metallic, 398.
 simple, 398.
 Cyanobenzene, 476, 482.
 Cyanohorm, 395.
 Cyanogen, 39.
 chlorids, 393, 398, 402, 414.
 compounds, 391.
 hydrid, 391.
 iodid, 388.
 sulfhydrate, 396.
 Cyanophenin, 537.
 Cyclic compounds, 272, 433.
 Cyclodolefin, 434.
 Cycloheptatriene, 552.
 Cycloheptene, 552.
 Cyclohexadiene, 486.
 Cyclohexane, 486.
 Cyclohexene, 434, 486.
 Cycloparaffins, 434.
 Cyclopterin, 589.
 Cyclotriolefin, 434.
 Cymene, 442, 447, 492.
 Cymogene, 276.
 Cymylic phenol, 447.
 Cystein, 421, 580, 581.

- Cystin, 374, 416, **421**, 579, 580, 581, 595, 596,
 617, 640, 757, 759.
 Cystinuria, 422, 757, 758.
 Cytolysins, 657, **671**, 675.
 Cytolysis, 656.
 Cytosin, **526**, 593.
 Cytotoxins, 657, 670, **671**.

 Dahlia, 506.
 Dambonite, 490.
 Dambose, 490.
 Daphnetin, 466.
 Daphnin, 466.
 Deamidation, 413.
 Decahydroquinolin, 544.
 Decompositions, 62.
 double, 62.
 primary, 63.
 Degrees of freedom, 94.
 Dehydromorphin, 563.
 Deliquescence, 27.
 Denaturized proteins, 575.
 Density, 9, 10.
 absolute, 9.
 critical, 30.
 current, 43.
 normal electric, 45.
 relative, 10.
 Deoxidation, 108.
 Deoxystrychnin, 560.
 Deuteroalbumoses, 614, **616**, 618, 629.
 Deuteroelastose, 597.
 Dextrin, 287, 321.
 Dextrins, 321.
 Dextrogyrous substances, 38.
 Dextrose, 314.
 Diabetes, 744, **745**, 746, 748, **753**.
 pancreatic, 746.
 phloridzin, 744.
 Diabetic sugar, 314.
 Diacetamid, 400.
 Diacetin, 296.
 Diacetamin, 409.
 Diacetylene series, 273.
 Diacetylenediamin, 514.
 Diacetylmorphin, 562.
 Diacipiperazin, 416, 522.
 Diacipiperazins, 522.
 Diacydylureids, 407.
 Dialdehydes, **306**, 335.
 Dialysis, 18.
 Diamid, 152, 484.
 aspartic, 407.
 Diamidodiphenol, 439.
 Diamidoparaffins, 387.
 Diamids, 399, 401.
 dialkyl, 379.
 mononalky, 379.
 primary, 403.
 Diamin diacetylene, 385, 514.
 diethylen, 522.
 dimethylp enylene, 520.
 diphenyldiethylene, 522.
 ethylene, 385.
 h xamethylene, 386.
 pentamethylene, 386, 387, 519.
 tetramethylene, 385, 386.
 tetramethylmethylene, 380.
 triethylene, 385.
 trim thylen, 385, 386.
 Diamins, 302, 366, 377, 378, 380, 382, **385**,
 386, 395, 408, 581.

 Diamond, 188.
 Diastase, 287, 319, 605.
 pancreatic, 627, **631**, **643**.
 Diastatic action, 605.
 Diazins, 520.
 Diazo amidobenzene, 482, 484.
 amido compounds, 481, **482**, 483, 484.
 benzene, 481.
 chlorid, 481, 482, 484, 501.
 cyanid, 482.
 compounds, 380, 444, 471, **481**, 484, 488.
 dyes, 484.
 group, 481.
 oxy compounds, 482.
 paraffins, 376.
 reaction, 479.
 Diazoles, 511, 512.
 Diazotizing, 482.
 Dibenzopyrones, 539.
 Dibenzopyrrole, 543.
 Dibenzoyl, 504.
 Dibenzyl, 502.
 Dibrommethyl bromid, 280.
 Dibromobenzenes, 438.
 Dibromoparaffins, 434.
 Dibromopropylin, 427.
 Dibutyldiacipiperazin, **522**.
 Dibutyraldin, 550.
 Diacodyl, 422.
 Dichloranilin, 475.
 Dichlorethane, 299.
 Dichlorethylbenzene, 463.
 Dichlorhydrin, 426.
 Dichlormethane, 278.
 Dichlormethyl chlorid, **278**.
 Dichloronaphthalene, 496.
 Dichloropropane, 299.
 Dicyanids, 335, 395.
 Dicyanogen, 395, 396.
 Diethylacetamid, 399.
 Diethylbenzenes, 441.
 Diethylcarbinol, 293.
 Diethylenediamin, 522.
 Diethylmalonylurea, 526.
 Diffusion of gases, 20.
 of liquids, 18.
 Difluordiphenyl, 502.
 Digestion, 599, **606**.
 autolytic, 606.
 Diglycerids, 296.
 Diglycylglycin, 416.
 Digitaliresin, 467.
 Digitalis glucosids, 467.
 Digitalin, 467.
 Digitalose, 467.
 Digitogenin, 467.
 Digitonein, 467.
 Digitonin, 467.
 Digitoxin, 467.
 Dihydrobenzenes, 434, **486**.
 Dihydrocymenes, 487.
 Dihydrofurfuran, 509.
 Dihydroglyoxalins, 514.
 Dihydropyrazole, 512.
 Dihydropyridins, 519, **523**.
 Dihydropyrrole, 511.
 Dihydroquinolins, 544.
 Dihydrostrychnolin, **560**.
 Dihydrotropan, 552.
 Diimins, 357, 382.
 Diindoxyl, 542.
 Diiodomethyl iodid, 280.

- Dihydrothymol, 447.
 Diketones, 307, 308, 499.
 Diketopurin, 532.
 Diketotetrahydroglyoxalin, 515.
 Diketotetrahydropyrimidin, 523.
 Dimetadioxytoluene, 449.
 Dimethoxyisoquinolin, 565.
 Dimethyl acetone hydrazone, 382.
 amidobenzene, 621, 622.
 amin, 381.
 anilin, 302, 503, 505.
 anthracene, 497.
 arsin, 422.
 benzenes, 441, 442.
 carbinamin, 382.
 ethylbenzenes, 441.
 Dimethylia, 381.
 Dimethyl indoles, 540.
 ketone, 307.
 malonylurea, 526.
 oxamid, 379.
 oxyphthalid, 462.
 phenols, 446.
 phenylenediamin, 520.
 pyrazole, 512.
 pyridins, 518.
 uracil, 524.
 xanthins, 533.
 Dimorphism, 17.
 Dinitranilins, 475.
 Dinitrobenzenes, 440, 471.
 Dinitroresols, 472.
 Dinitronaphthols, 498.
 Dinitrophenols, 472.
 Dinitrosoresorcinol, 473.
 Diolefins, 273, 425.
 Diols, 294.
 Dionin, 562.
 Dioses, 309, 310.
 Dioxindole, 478, 541.
 Dioxycetone, 296, 310.
 Dioxyanthracenes, 499.
 Dioxyanthraquinone, 500.
 Dioxycoumarin, 467.
 Dioxymethylanthraquinone, 500.
 Dioxypurin, 532.
 Dioxyracil, 529.
 Dipentene, 487, 488, 491.
 nitrosochlorid, 487.
 Dipetids, 412, 416.
 Diphenyl, 496, 501.
 acetylene, 502, 503.
 benzene, 501.
 diacetylene, 503.
 diethylenediamin, 522.
 Diphenylene diketone, 496.
 diphenylethylene, 494.
 imid, 538.
 ketone, 499.
 methane, 494.
 sulfid, 501.
 Diphenyl ethanes, 502.
 ethylene, 502, 503.
 hydrazin, 484.
 imid, 543.
 methane, 439, 494, 502.
 olefins, 502.
 oxid, 464, 501.
 paraffins, 502.
 phthalid, 504.
 pyridins, 545.
 Dipiperidin, 519.
 Dipyrrolyl, 545.
 Disaccharids, 309, 316, 643.
 Disacryl, 427.
 Disdiazamido compounds, 482.
 Displacement, 87.
 Dissociation, 70, 90, 115.
 coefficient of, 73.
 constant, 75.
 degree of, 73.
 Distillation, 32.
 fractional, 51.
 Disulfids, 371.
 Dithioketones, 373.
 Diureids, 406.
 Divisibility, 3.
 Dolomite, 240, 241.
 Dulcin, 298.
 Dulcitan, 298.
 Dulcite, 298, 315.
 Dulcitol, 298, 346.
 Dulcose, 298.
 Dutch liquid, 364, 424.
 Dynamite, 365.
 Dyne, 7.
 Dyalysin, 635, 640.
 Ebullition, 29.
 Ecoboln, 569.
 Ecgonin, 519, 548, 552, 553, 555.
 Edestin, 587.
 Efflorescence, 17.
 Eggs, white of, 584.
 yolk of, 586.
 Ehrlich's diazo reaction, 743.
 theory, 672.
 Elastin, 583, 596, 619.
 Elastoses, 619.
 Elayl, 423.
 chlorid, 364.
 Electric circuit, 40.
 conductance, 41.
 conductivity, 41.
 of blood, 658, 676.
 of urine, 699.
 current, 40.
 quantity, 41, 44.
 resistance, 41.
 resistivity, 41.
 units, 44.
 Electricity, 39.
 galvanic, 40.
 negative, 39.
 positive, 39.
 resinous, 39.
 vitreous, 39.
 Electrodes, 40.
 Electrochemical equivalent, 71.
 Electrolysis, 43, 62.
 Electrolyte, 43.
 Electrolytic dissociation, 70.
 Electromotive force, 41.
 Electronegative, 62.
 Electropositive, 62.
 Elements, 47, 55.
 acidulous, 101, 128.
 amphoteric, 101, 193.
 basulous, 102, 215.
 classification of, 100, 103.
 electronegative, 62, 101.
 electropositive, 62, 102.
 typical, 101, 105.
 Eleoptenes, 488.

- Eleutiation, 238.
 Emerald, 245.
 green, 195.
 Emery, 246.
 Emetin, 570.
 Emodin, 500.
 Emulsin, 465, 466, 468, 606.
 Emulsion, 366.
 Energy, 8, 598.
 chemical, 86.
 dissipation of, 9.
 kinetic, 8.
 potential, 9.
 Enol form, 537.
 Enterokinase, 626, 627.
 Enzymes, 599, 603.
 amylolytic, 605.
 autolytic, 631.
 classification of, 605.
 coagulating, 606.
 glucosid-splitting, 606.
 glycolytic, 606.
 lipolytic, 605.
 mineral, 604.
 of plasma, 654.
 proteolytic, 581, 605.
 salivary, 607.
 Eosin, 451.
 Epichlorhydrin, 351.
 Epiguanin, 532, 536.
 Episarkin, 532, 536.
 Epsom salt, 241.
 Equations, 60.
 Equilibrium, 30.
 apparent, 88.
 chemical, 87.
 heterogeneous, 88, 93.
 homogeneous, 88.
 metastable, 95.
 nitrogenous, 707.
 real, 88.
 Equivalent, 64.
 chemical, 60.
 conductivity, 74.
 electrochemical, 71.
 Joule's, 23.
 osmotic, 18.
 Erbium, 55, 103.
 Erepsin, 632.
 pancreas, 630.
 Ergotin, 569.
 Erythrin, 297.
 Erythrite, 297.
 Erythrodestrin, 322, 643.
 Erythroglucin, 297.
 Erythrol, 297, 345, 509.
 triacetyl, 367.
 tetranitro, 297, 367.
 Erythrololysis, 656.
 Erythrose, 310.
 Eserin, 570.
 Essence of Mirbane, 471.
 of turpentine, 488.
 Essences, 366, 486, 488.
 Ester, acetoacetic, 360, 513, 524, 529, 719.
 alkaloids, 547, 552, 553.
 amidoacetoacetic, 420.
 benzoylactic, 525.
 cyanoacetic, 534, 535.
 cyanomalonie, 395.
 cyanopropylmalonic, 418.
 diethylxamic, 403.
 dimethylxamic, 379.
 formic, 420.
 formylhippuric, 420.
 glycerolformic, 426.
 glycocoll, 522.
 hippuric, 420.
 malonamic, 411.
 malonic, 361, 482, 527.
 methenyltricarboxylic, 338.
 methylenemalonic, 430.
 monobenzoylserin, 420.
 nitroacetic, 412.
 phenylhydrazonacetic, 513.
 sodiumformylacetic, 524.
 sodiumpropylformic, 524.
 sulfates, 470, 646, 647, 684, 702, 728.
 Esters, 282, 284, 286, 294, 348, 358, 410.
 acetoacetic, 360, 361, 362.
 acid, 358.
 alcohol, 358.
 aromatic, 458.
 benzoic, 298.
 beta-ketonic, 347, 360.
 carbonic, 402.
 cyanic, 328.
 cyclic, 368.
 dioxymalonic, 347.
 haloid, 277, 286, 294, 359, 363, 393.
 hydrocyanic, 393.
 hyposulfurous, 360.
 isocyanic, 379, 397, 406.
 isothiocyanic, 397.
 ketonic, 347, 360, 361, 513.
 malonic, 361, 362.
 menthyl, 490.
 nitric, 379.
 nitrous, 376.
 of amidoacids, 412.
 of carbonic acid, 402.
 of cholesterol, 638.
 of dihydric alcohols, 363.
 of glycerol, 364, 365.
 of glycols, 294, 363.
 of ketone acids, 347, 360, 513, 523.
 of monocarboxylic acids, 379.
 of monohydric alcohols, 358.
 of oxyacids, 368.
 of polyhydric alcohols, 367.
 of trihydric alcohols, 364.
 oxymalonic, 347.
 phenol, 446.
 phenyl, 444, 446, 464.
 thiophosphoric, 371.
 sulfurous, 360.
 Ethane, 330, 423, 425.
 Ethene, 423, 425.
 chlorhydrin, 295.
 compounds, 424.
 glycol, 295.
 homologues of, 424.
 Ethenylamidoxim, 388.
 Ether, acetic, 360.
 allylic, 421.
 diethyleneglycol, 350.
 dimethylpyrocatechuic, 449.
 ethylic, 464.
 glycerol, 351.
 glycoldiethyl, 350.
 glycolethyl, 350.
 hydriodic, 281.
 hydrobromic, 281.
 hydrochloric, 281.

- Ether, methylphenyl, 444, 464.
 monomethylpyrocatechuic, 448.
 muriatic, 281.
 nitric, 359.
 nitrous, 359.
 petroleum, 276.
 phenyl, 464.
 propargylethyl, 431.
 pyroacetic, 307.
 pyrocatecholmethylene, 450.
 sulfuric, 349, 359.
 Ethers, 348.
 benzenic, 443.
 compound, 348, **358**.
 cyclic, 350.
 glycerol, 350.
 glycol, 350.
 haloid, 277.
 mixed, 282, 348.
 phenyl, 446.
 simple, 282, **348**.
 Ethidene chlorid, 299, **424**, 425.
 compounds, 424.
 diethylsulfone, 373.
 hydroxylamin, 409.
 Ethine, 424.
 Ethol, 363.
 Ethyl acetamid, 401.
 acetate, **360**, 361, **400**, 401.
 acetoacetate, 360.
 acetylsodacetate, 361.
 amidoacetate, 414.
 amin, 381, 394, 401.
 benzene, 441, **442**.
 borate, 187.
 bromid, **281**, 423, 424.
 carbinol, 291.
 chlorid, **281**, 303, 364.
 cyanid, 394.
 dimethylcarbinol, 294.
 hydroxid, 287.
 iodid, **281**, 424, 472.
 isocyanate, 397.
 malonate, 361.
 mercaptan, 372.
 mercaptoketopyrimidins, 524, 525.
 mercaptopol, 374.
 methylcarbinol, 292.
 methylpyridin, 559.
 morphin, 562.
 nitrate, 359.
 nitrite, 359.
 orthocarbonate, 388.
 oxalate, 403.
 oxid, 349.
 phenols, 447.
 pyridins, 518.
 pseudourea, 524.
 sulfates, 359, 360.
 sulphydrate, 372.
 sulfid, 579, 580.
 sulfites, 360.
 thallin, 544.
 urethan, 402.
 Ethylates, 289.
 Ethylene, 364, **423**.
 benzene, 442.
 bichlorid, 364.
 bromid, 295, **424**, 522.
 chlorhydrin, 350, **363**, 383.
 chlorid, **364**, 424.
 compounds, 424.
 Ethylene, cyanhydrin, 342.
 cyanid, 385.
 diamin, 385.
 diammonium chlorid, 514.
 halids, 423.
 hydroxamin, 409.
 imid, 508.
 imin, 387.
 monochlorid, 314.
 naphthalene, 495.
 oxid, 350.
 sulfid, 508.
 Ethylidene compounds, 424.
 Eucalypteol, 490.
 Eucalyptol, 490.
 Eugenol, 450.
 Euglobulin, 652.
 Euphorin, 402.
 Evaporation, 49.
 Exalgin, 476.
 Exudates, 693.
 Fæces, 546, **647**.
 Fahrenheit's scale, 22.
 Faraday, 72.
 Fats, 366, 633, 644, 645, 654, 693.
 phosphorized, 367.
 Feldspar, 245, 248.
 Ferments, **699**, 603.
 Fermentation, acetous, 601, 643.
 alcoholic, **600**, 643.
 ammoniacal, 601.
 butylic, 601.
 butyric, 331, 601, 643.
 lactic, 298, 601, 643.
 mixed, 601.
 mucic, 298.
 Fermentations, bacterial, 601.
 Ferrates, 199.
 Ferric acetates, 202.
 bromid, 200.
 chlorid, 200.
 citrate, 202.
 ferrocyanid, 203.
 hydrates, 198.
 iodid, 200.
 nitrates, 201.
 oxid, 198.
 pyrophosphate, 201.
 sulfates, 200, 201.
 sulfid, 199.
 tartrate, 202.
 Ferrocyanids, 399.
 Ferrous acetate, 201.
 bicarbonate, 202.
 bromid, 200.
 carbonate, 202.
 chlorid, 199.
 ferricyanid, 203.
 hydrates, 198.
 iodid, 200.
 lactate, 202.
 nitrate, 201.
 oxalate, 202.
 oxid, 198.
 phosphates, 201.
 sulfate, 200.
 sulfid, 199.
 tartrate, 202.
 Fibrin, **651**, 668.
 ferment, 652.
 Fibrinogen, 582, 585, **651**, 668, 669, 692.

- Fibrinoglobulin, 585, 588, 589, 609.
 Fibrinoplastic substance, 552.
 Fibrinoses, 613.
 Fibroin, 420, 583, 597.
 Fire-damp, 275.
 Flavanilin, 475.
 Fluorene, 493, 494, 497, 499, 501, 502.
 ketone, 499.
 Fluorescein, 449, 451.
 Fluorin, 125, 126.
 Fluor spar, 126.
 Foot-pounds, 8.
 Force, 2.
 chemical, 86.
 electromotive, 41.
 Formaldehyde, 300 (see Aldehyde, formic).
 Formaline, 301.
 Formals, 302, 306.
 Formamid, 400.
 Formin, 409.
 Formonitril, 329, 331, 336.
 Formose, 301, 314.
 Formoxim, 410.
 Formulae, 60.
 algebraic, 264.
 empirical, 84.
 general, 264.
 graphic, 86, 263.
 rational, 85.
 typical, 85.
 Formyl bromid, 290.
 chlorid, 278.
 hydrid, 300.
 iodid, 280.
 Fractional distillation, 51.
 Fraunhofer's lines, 35.
 Freezing point, 21, 68.
 of blood, 553, 676.
 of urine, 698.
 Fructosamin, 485.
 Fructose, 311, 315, 485, 681.
 Fruit sugar, 315.
 Fuchsin, 506.
 Fucose, 311.
 Furane, 517.
 Furazoles, 511.
 Furfurane, 507, 508, 509.
 Furfurole, 310, 323, 509.
 Furole, 509.
 Furomonazoles, 512.
 Fusel oil, 291, 292.
 Fusing point, 26.
 Fusion, 26.
 heat of, 26.

 Gadinin, 375.
 Gadolinium, 55, 102, 103.
 Galactose, 311, 315, 319.
 Galena, 204, 208.
 Gallein, 450.
 Gallisin, 314, 319.
 Gallium, 55, 102, 103, 245.
 Galvanic battery, 40.
 cell, 40.
 circuit, 40.
 Garnet, 245.
 Gas, ideal, 20.
 tar, 440.
 Gases, 19, 29.
 absorption of, 21.
 diffusion of, 20.
 effusion of, 20.

 Gases, expansion of, 23.
 general law of, 24.
 kinetic theory of, 25.
 mixtures of, 20, 49.
 Gasolene, 276.
 Gastric digestion, 608.
 juice, 608, 609.
 abnormal variations of, 609.
 acetic acid in, 619.
 acetone in, 620.
 acid of, 609.
 action on proteins, 612.
 anachlorhydria in, 619.
 analysis of, 620.
 arsenic in, 620.
 bile in, 620.
 butyric acid in, 609, 620, 624.
 fermentation, effect on, 609.
 free acid of, 609, 620.
 haematin in, 620.
 hydrochloric acid in, 609, 620, 621.
 effective, 623.
 hyperchlorhydria of, 619.
 hypochlorhydria of, 619.
 lactic acid in, 620, 623.
 morphin in, 620.
 native albumins in, 624.
 organic acids in, 609, 620, 623, 624.
 pepsin in, 610, 624.
 pepsinogen in, 610, 624.
 pepsohydrochloric acid in, 611.
 peptones in, 624.
 primary albumoses in, 624.
 products of digestion in, 624.
 protein hydrochloric acid in, 622, 623.
 serum albumin in, 624.
 syntonin in, 624.
 total acidity of, 620.
 urea in, 620.
 mucus, 608.
 Gastrosteapsin, 619.
 Gelatin, 580, 596, 619, 628.
 explosive, 323.
 peptones, 596.
 sugar, 413.
 Gelatinoses, 612.
 Gelatoses, 596, 619.
 Geneva commission, 271.
 Geraniol, 427, 428.
 Germanium, 55, 102, 103.
 Glass of antimony, 185.
 soluble, 219.
 Glauber's salt, 218.
 Gliadin, 587.
 Globin, 522, 588, 630, 660.
 Globulinoses, 613.
 Globulins, 502, 583.
 Glonoin, 364.
 Glucose, 655.
 Glucinum, 55, 103.
 Glucoalbumose, 613, 614, 615, 618.
 Gluconolactone, 343.
 Glucononitril, 343.
 Glucosamin, 487, 581, 594.
 Glucosamins, 387.
 Glucose, 287, 311, 314, 368, 465, 485, 644,
 654, 679, 680, 744, 745, 747, 749, 750.
 diacetic, 368.
 tetracetic, 368.
 triacetic, 368.
 Glucoses, 311.
 Glucosids, 311, 314, 368, 464, 465.

- Glucososazone, 315, 388, **485**.
 Glucosyl phenate, 368, 465.
 Glucovanillin, 466.
 Glucuronates, 646.
 Glutamin, 420.
 Gluten, 587.
 casein, 587.
 fibrin, 587.
 protein, 582, 586.
 Glutenin, 587.
 Glutokyrin, 629.
 Glycerids, 296, 364.
 Glycerin, 339.
 Glycerol, 287, 295, **296**, **426**, **427**, **552**.
 aldehyde, 299, 310.
 halohydrins, 364.
 ketone, 299, 310.
 trinitrate, 364.
 Glycerols, 295.
 Glycid, 351.
 Glycin, 413.
 Glycogen, 319, **321**, 643, 654, 679, 680, 681, 682, 745.
 Glycocoli, **314**, 479, 529, 530, 580, 596, 606, 614, 630, 634, 636, 639, 640, 680, 685, 724, 756, 763 (see acid, amidonacetic).
 trimethyl, 384.
 Glycocols, 412.
 Glycol chlorhydrins, 364.
 ethene, **298**, 424.
 ethylene, 295.
 halohydrins, 313.
 methene, 294.
 propyl, 337.
 toluylene, 504.
 Glycollid, 412.
 Glycols, **294**, 339, 364.
 ethers of, 299, 310.
 Glycolyl aldehyde, 299, 310.
 diurea, 414, **515**.
 urea, 414, **515**.
 Glycoproteids, 387, 583, **595**.
 Glycosuria, 467, 625, 682, 683, **744**, **745**.
 alimentary, 683.
 pancreatic, 683.
 phloridzin, 682.
 Glycylalanin, 416.
 Glycylglycin, 416.
 Glyoxal, **406**, 341, 514.
 methyl, 308.
 Glyoxalldina, 514.
 Glyoxalin, 306, **514**.
 Glyoxals, 299.
 Gold, 193.
 fulminating, 396.
 trichlorid, 193.
 Gram, 6.
 calorie, 22.
 equivalent, 60, 64.
 molecule, 57.
 Granulose, 321.
 Grape sugar, 314.
 Graphite, 188.
 Gravity, 6.
 specific, 10.
 Groups, characterizing, 270.
 Guaiacol, 446, **448**.
 Guanid, cyanacetic, 534, 535.
 Guanidin, **388**, 398, 403, 418, 527, **534**, **535**, 579, 580, 631.
 Guanidins, substituted, 388.
 Guanids, 522, **527**.
 Guanin, 388, 532, **534**, 593, 724.
 Guano, 237.
 Guarantin, 533.
 Gulose, 311.
 Gum resins, 493.
 Gums, 321.
 Gun cotton, 323.
 powder, 224.
 Guvacin, 549.
 Gypsum, 237.
 Hæmatin, 641, **663**.
 Hæmatite, 197.
 Hæmatocrit, 650.
 Hæmatoidin, 636, 641, **665**.
 Hæmatoporphyrin, 641, 664, **665**, 725, 741.
 Hæmaturia, 741.
 Hæmin, 663, **664**.
 Hæmochromogen, 663, **664**.
 Hæmocytolysis, 656.
 Hæmoglobin, 641, **659**, 676, 679, 689, 741.
 carbon dioxide, 663.
 carbon monoxid, 662.
 Hæmoglobinometers, 677.
 Hæmoglobins, 583.
 Hæmoglobinuria, 641, 741.
 Hæmolysins, 671.
 Hæmolysis, 656, **671**.
 Hæmopyrrole, 510, 637.
 Halogens, 125.
 Halohydrins, 382.
 glycerol, 364.
 glycol, 363.
 Haptophores, 673, 674.
 Hausmannite, 195.
 Heat, 21, 46.
 atomic, 55.
 dynamic theory of, 24.
 effects of, 21.
 expansion by, 23.
 latent, 26.
 of vapor, 33.
 measure of, 22.
 mechanical equivalent of, **22**.
 molecular, 58.
 of combustion, 99.
 of dissociation, 100.
 of formation, 99.
 of fusion, 26.
 of neutralization, 100.
 of precipitation, 98.
 of reaction, 99.
 of solution, 98.
 of vaporization, 33.
 quantity of, 21.
 specific, 33.
 Heavy spar, 239.
 Helium, 55, 101, 103, 125.
 Hemi group, 612, 618.
 Hemihedral crystals, 16.
 Hemiterpenes, 487.
 Heptoses, 309, 310, 600.
 Heroin, 562.
 Heteroalbumose, **613**, 614, 618.
 Heterocyclic compounds, 272, **433**, **507**.
 Heteroxanthin, 532, **533**, 724.
 Hexacarboeyclic compounds, 434, 435.
 Hexachlorethane, 281.
 Hexaglycylglycin, 416.
 Hexahydrobenzene, 434, 439, **486**.
 Hexahydrocymene, 489, 490.
 Hexahydrophenol, 491.

- Hexahydropyrazin, 520, 522.
 Hexahydropyridins, 518, 519.
 Hexahydropyrimidin, 523.
 Hexamethylene, 434.
 tetramin, 301, 409.
 Hexites, 298.
 Hexon bases, 403, 417, 516, 579, 581, 589.
 Hexones, 417.
 Hexoses, 298, 301, 309, 310, 311, 600.
 Histidin, 417, 516, 589, 596, 589, 633.
 Histon, 588, 592.
 nucleates, 591.
 Histons, 582, 587, 589.
 Hoffman's violet, 506.
 Homatropin, 555.
 Homologous series, 264.
 Horn lead, 304.
 Horse-power, 46.
 Hydantoin, 406, 516.
 Hydracetic, 486.
 Hydracids, 64.
 Hydramins, 378, 382, 406, 581.
 Hydrastin, 463, 548.
 Hydrates, 115.
 Hydrasids, 390, 410.
 Hydrazin, 152, 389, 390.
 compounds, 484.
 hydrate, 512.
 sulfate, 389.
 Hydrazins, 390, 471.
 aromatic, 484.
 Hydrazobenzene, 483, 484.
 Hydrazo compounds, 483.
 Hydrazones, 299, 482, 484, 491, 499, 513.
 aldehyde, 410.
 ketone, 410.
 Hydrindene, 494.
 Hydrindones, 499.
 Hydron, 76.
 Hydroaromatic compounds, 486.
 Hydrobenzoin, 504.
 Hydrobilirubin, 637.
 Hydrocarbons, 265, 271, 273, 439.
 acetylene series, 273, 424.
 aliphatic, 273.
 condensed, 493, 494.
 diacetylene, 273.
 diolefin, 273, 245.
 ethene series, 273, 423.
 ethine series, 273, 423.
 heptacarbo-cyclic, 434.
 hexacarbo-cyclic, 434.
 hydroaromatic, 486.
 hydrobenzenic, 439.
 methane series, 273.
 monobenzenic, 440.
 olefin-acetylene, 273.
 olefin series, 273, 423.
 pentacarbo-cyclic, 434.
 saturated, 273, 434.
 tetracarbo-cyclic, 434.
 tricarbo-cyclic, 434.
 Hydrocele, fluid of, 693.
 Hydrocotarnin, 564, 566.
 Hydrogen, 105, 113.
 antimonid, 183.
 arsenid, 170, 175, 640, 641.
 bromid, 134.
 chlorid, 130.
 cyanid, 391.
 dioxid, 123.
 fluorid, 126.
 Hydrogen, iodid, 136.
 nitrate, 157.
 nitrid, 151.
 pentasulfid, 141.
 peroxid, 123, 604.
 phosphids, 165.
 polysulfids, 191.
 silicid, 191.
 sulfate, 144.
 sulfid, 139.
 Hydrolysis, 116.
 Hydronaphthalenes, 495.
 Hydropyridins, 519.
 Hydropyrimidins, 522.
 Hydropyrroles, 511.
 Hydroquinolins, 544.
 Hydroquinone, 449, 606, 647.
 Hydrosulfids, 141.
 Hydroterpenes, 489.
 Hydrouracil, 523.
 Hydroxamins, 362.
 Hydroxidion, 76.
 Hydroxids, 64, 115.
 basic, 115.
 hydrocarbon, 284.
 Hydroxyl, 64, 76, 269, 369.
 alcoholic, 369, 370.
 phenolic, 369, 370.
 Hydroxylamin, 152, 299, 388, 409.
 compounds, 376.
 aromatic, 473.
 Hydroxylamins, 408.
 Hygrins, 546, 548.
 Hygrometer, 150.
 Hyoscin, 548, 552, 555.
 Hyoscyamin, 548, 552, 554.
 Hyperchlorhydria, 619.
 Hyperglykæmia, 683, 745, 746.
 Hyperisotonic, 657.
 Hypnone, 455.
 Hypochlorhydria, 619.
 Hypophosphites, 167.
 Hypoxanthin, 532, 533, 534, 536.
 Iceland spar, 237.
 Ichthulin, 586.
 Ichthylepidin, 583, 597.
 Ichthyol, 374.
 Idose, 311.
 Imidazole, 514.
 Imido group, 380.
 Imidoparaffins, 377.
 Imids, 387, 401, 408.
 Imin bases, 377.
 Imins, 357.
 Immune body, 672.
 Immunity, 669.
 acquired, 670.
 active, 670.
 natural, 670.
 passive, 670, 674.
 Impenetrability, 3.
 Indene, 493, 494.
 Indestructibility, 3.
 Index of refraction, 34.
 Indican, 467, 541, 542, 729.
 urinary, 541.
 Indicanin, 467.
 Indicanuria, 729.
 Indicators, 620.
 Indiglucin, 467.
 Indigo, 459, 472.

- Indigo blue, 467, 503, 541, **542**.
 carmine, 542.
 white, 542.
 Indigotin, 542.
 Indium, 55, 102, 103, 245.
 Indoanilin dyes, 452.
 Indole, 538, **539**, 540, 578, 579, **580**, **581**, **595**,
 596, 597, 614, 646.
 homologues, 540.
 Indone, 499.
 Indophenin, 510.
 Indoxyl, **541**, 542, **646**, 728.
 Indulin dyes, 450.
 Indulins, 520.
 Inertia, 4.
 Inosite, **489**, 753.
 Insolubility, 27.
 Insulators, 27.
 Intermediate body, 672.
 Intestinal concretions, 649.
 gases, 647.
 secretions, 632.
 Intestine, bacterial action in, **643**.
 chemical changes in, 642.
 putrefaction in, **643**, 702, 729.
 Inulase, 605.
 Inulin, 315, 321, 605.
 Inversion, **316**, 318.
 Invertase, 602, 605.
 Invertin, 465, 602, 632, **643**.
 Iodanilins, 475.
 Iodidion, 137.
 Iodids, 136.
 Iodin, 125, **135**.
 greens, 506.
 number, Hübl's, 429.
 oxacids of, 137.
 Iodoform, 281.
 Iodol, 511.
 Iodophenols, 448, 449.
 Iodopropane, 382.
 Iodoquinin sulfate, 557.
 Ionization, 70, 72.
 Ions, 39, 44, 64, 72, 83.
 Iridium, 213.
 Iron, 194, 197.
 acetates of, 201.
 bromids of, 200.
 chlorids of, 199, 200.
 citrate of, 202.
 dialysed, 199.
 galvanized, 243.
 group, 194.
 hydrates of, 198.
 in bile, 641.
 iodids of, 200.
 magnetic oxid of, 198.
 nitrates of, 201.
 oxids of, 198.
 phosphates of, 201.
 reduced, 198.
 salts of, 200.
 spathic, 202.
 sulphs of, 199.
 tartrates of, 202.
 Ironstone, 197.
 Isatin, 458, 479, 510, **541**, 542.
 Isatoxin, 542.
 Isinglass, 596.
 Isoacetonitril, 394.
 Isoalcohols, 285.
 Isobenzonitril, 394, **476**.
 Isobutylcarbinol, 639.
 Isocholin, **383**, 385.
 Isocoumarin, 539.
 Isocyanates, 396.
 Isocyanids, 380, 394, 401.
 Isodipyridin, 551.
 Isodulcite, 311.
 Isoglucosamin, 388.
 Isoindole, **538**, 541.
 Isomaltose, 314, **319**, 607, **643**.
 Isomerism, 265, 436.
 place, 339, 412.
 position, 339.
 space, 311, 430.
 stereo, 311.
 Isomorphism, 16.
 Isonicotin, 545.
 Isonitrils, 380, 394.
 Isopelletierin, 549.
 Isoprene, 426.
 Isopropylamin, 382.
 Isopropylbenzene, 441.
 Isopyrazolon, 512.
 Isoquinolin, 538, **544**.
 alkaloids, 548, **562**, **565**.
 Isoserin, 417, **430**.
 Isosmotic, 67.
 Isotonic coefficient, 657.
 Ivory black, 189.
 Jaborandin, 556.
 Jaborin, 549, 556.
 Japaconin, 569.
 Japaconitin, 569.
 Javelle water, 224.
 Jecorin, 654.
 Jervin, 570.
 Joule, 8.
 Joule's equivalent, 23.
 Juvacin, 548.
 Kairin, 544.
 Kathode, 42.
 Kations, 44.
 Kelp, 135.
 Keratins, 583, **595**.
 Keratinoses, 602.
 Kermes mineral, 185.
 Kerosene, 276.
 Ketohydrazones, 382, **485**.
 Ketohydrocymenes, 491.
 Ketohydroglyoxalins, 515.
 Ketols, 308, 309.
 Ketomenthadiènes, 491.
 Ketomenthans, 491.
 Ketomenthenes, 491.
 Ketone acids, 339, 340, **347**.
 alcohols, 299, **308**.
 dimethyl, 307.
 diphenyl, 504.
 diphenylene, 499.
 fluorene, 499.
 form, 537.
 glycerol, 310.
 halids, 278.
 hydrazones, 410.
 methylphenyl, 463.
 naphthylmethyl, 499.
 phenylmethyl, 455.
 pimelin, 491.
 Ketones, 282, 283, 284, 286, 298, **307**, **324**, **325**,
 326, 339, 340, 391, 398, **409**, **424**, 517.

- Ketones, acetylene, 428.**
 aromatic, 455.
 benzenic, 443.
 camphan, 491, 492.
 cyclic, 335.
 diphenyl, 503.
 hydroaromatic, 489, 491.
 naphthyl, 499.
 olefin, 428.
 terpan, 491.
Ketopentoses, 310.
Ketopiperazines, 522.
Ketopiperidins, 413.
Ketopurins, 531, 532, 533.
Ketopyrimidins, 524.
Ketoses, 309, 310, 321, 325, 326, 485.
Ketoxims, 379, 383, 409, 410, 491.
Kilogram, 779.
Kilojoule, 23.
Kilometer, 1, 778.
Kilowatt, 46.
King's yellow, 174.
Knall-gas, 45.
Knock-out-drops, 305.
Koprostearin, 642.
Kornein, 597.
Krypton, 55, 101, 105, 125.
Kyanol, 473.
Kynurin, 544.
- Labarraque's solution, 220.**
Labile substances, 87.
Labradorite, 48.
Laccase, 606.
Laccol, 606.
Laemoid, 449.
Lactalbumin, 582, 764.
Lactam, methylguanidinacetic, 390.
Lactamid, 411, 414.
Lactams, 384, 412, 478.
Lactase, 632.
Lactids, 368, 412.
Lactine, 318.
Lactoglobulin, 582, 764.
Lactometer, 762.
Lactone, gluconic, 369.
Lactones, 314, 340, 343, 368, 428, 462, 500, 504.
Lactose, 316, 318, 600, 643, 644, 681, 752.
Lævogyrous substances, 38.
Lævulose, 315, 752.
Lalose, 752.
Lampblack, 189.
Lanolin, 638.
Lanthanum, 55, 102, 103.
Lapis infernalis, 231.
Laughing gas, 153.
Laue's violet, 520.
Law, Boyle-Mariotte, 19, 25, 26, 31.
 Dalton's, 20.
 Dalton-Gay Lussac, 23.
 Faraday's, 44.
 of Ampère, 52.
 of Avogadro, 52.
 of Charles, 23.
 of Dalton, 49.
 of definite proportions, 48.
 of Faraday, 71.
 of Guldberg and Waage, 93.
 of multiple proportions, 49.
 of Raoult, 68.
 of reciprocal proportions, 49.
- Law of Richter, 48.**
 of Van't Hoff, 89.
 of Wenzel, 49.
 Ohm's, 42.
 periodic, 102, 104.
Laws, Berthollet's, 77.
 Gay Lussac's, 52.
 Newton's, 4.
- Lead, 204.**
 acetates, 206.
 black, 188.
 carbonate, 206.
 chlorid, 206.
 chromate, 206.
 dioxid, 206.
 glycocholate, 635.
 group, 204.
 iodid, 206.
 monoxid, 206.
 nitrates, 206.
 orthonitrate, 206.
 oxide, 206.
 oxychloride, 206.
 pyronitrate, 206.
 red, 206.
 salts of, 206.
 subacetate, 206.
 sulfate, 206.
 sulfid, 206.
 taurocholate, 635.
 white, 207.
- Leads, electric, 40.**
Leather, 596.
LeChatelier, theorem of, 88.
Lecithalbumin, 588.
Lecithins, 367, 383, 584, 596, 631, 634, 644, 654, 666.
Legumin, 587.
Lepidin, 559.
Lepidins, 544.
Lethol, 363.
Leucanilins, 505.
Leucin, 414, 467, 479, 580, 581, 595, 596, 614, 617, 626, 633, 685, 757, 758, 763.
Leucinimid, 522, 630.
Leucins, 414.
Leucocytes, 656, 666.
Leucomalins, 390, 570, 571.
Leucomalachite green, 505.
Leuconuclein, 592, 669.
Leucopararosanilin, 503.
Leucylleucin, 416, 522, 630.
Leucylprolin, 511.
Levigation, 238.
Leyden crystals, 387.
Lichenin, 321.
Lieberkühn's jelly, 590.
Light, 34.
 chemical effects of, 39.
 dispersion of, 34.
 refraction of, 34.
 wave-lengths of, 36.
- Lime, 235.**
 milk of, 236.
 water, 236.
- Limonene, 487, 490.**
 tetrabromids, 487.
- Limestone, 235, 237.**
Linalool, 427, 488.
Linkages, 268.
Lipases, 605, 609, 619, 627, 631, 655.
Liquids, 18, 30.

- Liquids, diffusion of, 18.
 immiscible, 50.
 vapor tension of, 31.
 Liter, 1.
 Litharge, 205.
 Lithium, 215.
 bromid, 215.
 carbonate, 215.
 chlorid, 215.
 urates, 531.
 Liver, action on carbohydrates, 681.
 on fats, 681.
 on poisons, 678, 684.
 on proteins, 681.
 blood changes in, 678, 680.
 carbohydrates of, 679.
 fats in, 680.
 formation of ester sulfates, 684.
 of urea, 685, 720, 721.
 of uric acid, 684, 685, 721.
 glycogenic function of, 681, 682, 745.
 iron proteins in, 641, 679.
 proteins of, 679.
 sugar, 314.
 syntheses in, 680, 683.
 Loadstone, 198.
 Lucifer disease, 164.
 Lunar caustic, 231.
 Luteins, 586, 655.
 Lutidins, 518.
 Lycopotonin, 568.
 Lymph, 692.
 plasma, 692.
 Lyons blue, 506.
 Lysatinin, 419.
 Lysidin, 385, 514.
 urate, 531.
 Lysin, 403, 318, 480, 580, 581, 589, 595, 617,
 629, 633, 763.
 Lysins, 670, 671.
 Lysol, 446.
 Magenta, 506.
 Magnesia, 241.
 Magnesite, 241.
 Magnesium, 240.
 carbonate, 241, 242.
 chlorid, 241.
 group, 240.
 hydroxid, 241.
 oxid, 241.
 phosphates, 241.
 pyrophosphate, 241.
 sulfate, 241, 576.
 Malachite, 250.
 green, 505.
 Malonamid, 407, 411.
 Malononitril, 395.
 Malonyldimethylurea, 526.
 Malonylguanid, 527.
 Malonylurea, 522, 526, 529.
 Malt, 287.
 Maltase, 602, 603, 604, 607, 632, 655.
 Maltose, 287, 316, 319, 322, 600, 602, 604,
 607, 631, 643, 644, 681.
 Manganates, 196.
 Manganese, 194, 195.
 chlorids, 196.
 oxids, 196.
 salts, 196.
 Manganite, 195.
 Mannitan, 298.
 Mannite, 298.
 Mannitol, 298, 314.
 hexacetyl, 367.
 hexanitro, 368.
 Mannitols, 343.
 Mannose, 311, 314.
 Marble, 235, 237.
 Marsh gas, 275.
 Martius' yellow, 498.
 Mass, 5.
 action, 92.
 Massicot, 205.
 Matter, 2.
 states of, 13.
 Measures, 778.
 Meconin, 462, 564, 566.
 Meconium, 648.
 Meerschau, 240.
 Megohm, 46.
 Melam, 537.
 Melamin, 537.
 Melanin, 743.
 Melanins, 579, 597.
 Melanoidins, 579, 580.
 Melecitose, 319.
 Mellissin, 363.
 Melisyl palmitate, 363.
 Melitose, 319.
 Membranes, permeable, 18.
 semipermeable, 19.
 Menthadiene, 490.
 Menthane, 490.
 Menthen, 488, 490.
 Menthol, 489, 490, 491.
 Menthone, 491.
 Menthoxim, 491.
 Mercaptals, 373.
 Mercaptan, 371, 579, 646.
 Mercaptans, 371, 580.
 Mercaptids, 371, 372, 373.
 Mercaptol, 373.
 Mercurammonium chlorid, 258.
 Mercurdiammonium chlorid, 257.
 Mercuric chlorid, 257.
 cyanid, 259, 395.
 fulminate, 396.
 iodid, 258.
 nitrate, 259.
 oxid, 255.
 sulfate, 260.
 sulfid, 265.
 sulfochlorid, 257.
 Mercurous chlorid, 256.
 iodid, 258.
 nitrate, 259.
 oxid, 255.
 sulfate, 260.
 Mercury, 250, 254.
 chloramidid, 258.
 chlorids, 256.
 formamid, 401.
 fulminating, 396.
 iodids, 258.
 nitrates, 259.
 oxids, 255.
 phenate, 446.
 sulfates, 260.
 sulfids, 256.
 Meroquinene, 509.
 Mesityl oxid, 428.
 Mesitylene, 442.
 glycerol, 453.

- Mesoxalylurea**, 348, 527.
Metachloral, 303.
Meta compounds, 437.
Metadiasin 520, 521.
Metadioxybenzene, 449.
Metalbumin, 594.
Metalddehyde, 303.
Metallocyanids, 398.
Metals, 101, 102.
Metamerism, 265.
Metaphenylenediamin, 476.
Metatriasin, 536.
Metaxylene, 442.
Meter, 1, 778.
Methacetin, 477.
Methæmoglobin, 662.
Methane, 275.
 disulfethyldimethyl, 374.
 dithioethyldimethyl, 373.
 series, 273.
Methene chlorid, 278.
 dimethylate, 295, 306.
 glycol, 295.
 iodid, 301.
Methenyl, 275.
 chlorid, 278.
 iodid, 280.
Methine, 275.
Method, see Process, Test.
Methol, 363.
Methoxyl, 270.
Methyl, 275.
 acetamid, 476.
 acetylurea, 407.
 amidoacetate, 414.
 amin, 381, 414.
 anilin, 476.
 anthraquinone, 500.
 benzene, 439, 441.
 benzoylcyanhydrin, 463.
 benzoylecgonate, 556.
 blue, 506.
 bromid, 280.
 carbylamin, 394.
 chlorid, 278, 472.
 cyanid, 394, 401.
 dichloropyrimidin, 521.
 divinyl, 426.
 ethylbenzenes, 441.
 ethyl oxid, 348.
 ethylpyrimidin, 518.
 glycocoll, 389, 412, 414.
 glyoxalidin, 514.
 guanidin, 389.
 guanin, 536.
 heptenone, 428.
 hydantoin, 414, 515.
 hydrid, 275.
 hydroxid, 286.
 indoles, 486, 540, 541.
 iodid, 280, 311, 476, 513.
 isocyanid, 394.
 isopropylbenzenes, 441, 442.
 isopropylcarbinol, 294.
 isopropylphenols, 447.
 ketopurins, 532.
 morphin, 562, 564, 566.
 morphinmethine, 566.
 oxalate, 387.
 oxid, 349.
 penthioephene, 484.
 phenylhydrazin, 484.
 Methyl piperidin, 519.
 propylbenzenes, 441.
 propylcarbinol, 293.
 propylpyrrole, 510.
 pseudothiourea, 524, 525.
 purins, 528, 531.
 pyridina, 518.
 pyrimidin, 521.
 pyrroles, 510.
 quinin, 558.
 quinolins, 543, 544.
 tropidin, 552.
 uracils, 362, 521, 524, 525, 529.
 uramin, 389.
 urea, 407.
 xanthins, 526, 533.
Methylal, 295, 306.
Methylene, 275.
 blue, 506, 520.
 bromid, 495.
 chlorid, 278, 502.
 cyanid, 395.
 diethylsulfone, 373.
 diiodid, 373.
 iodid, 423.
 mercaptal, 373.
 oxids, 299.
Methylia, 381.
Mho, 46.
Mica, 240, 248.
Microhm, 46.
Microspectroscope, 36.
Milk, 617, 761.
 abnormal, 765.
 adulterations of, 765.
 analysis of, 766.
 casein in, 763.
 composition of, 762.
 corpuscles, 762.
 cows', 761, 765.
 human, 764.
 lactalbumin in, 764.
 lactoglobulin in, 764.
 physical properties of, 761.
 plasma, 763.
 reaction of, 761.
 salts of, 764.
 skimmed, 762.
 souring of, 761.
Milliampere, 44.
Mineral green, 252.
Minium, 205.
Miricyl hydroxid, 294.
Mixtures, isomorphous, 51.
 mechanical, 47, 54.
 of gases, 49.
 of liquids, 50.
 of solids, 51.
 of vapors, 49.
 physical, 49, 54.
Mol, 57.
Molasses, 317.
Molecule, 52, 53.
Molecular conductivity, 74.
 heat, 58.
 of vaporization, 58.
 theory, 52.
 volume, 57.
 weight, 56.
Molybdenum, 192.
Momentum, 7.
Monacetamid, 400.

- Monacetin, 296.
 Monoacidylureas, 406.
 Monamids, 379, 397, **399**.
 cyclic, 515.
 monacidyl, 406.
 primary, 399.
 secondary, 400.
 tertiary, 400.
 Monamins, 376, **377**, 378, 581.
 primary, 377, 378, **379**.
 secondary, 377, 379.
 tertiary, 377, 379.
 Monazoles, 51 512.
 Monobenzenic compounds, 456.
 Monobromocamphor, 492.
 Monochloranilins, 475.
 Monochloromethyl chlorid, 278.
 Monochlorobenzene, **442**, **444**.
 Monoglycerids, 296.
 Monohydrobenzenic compounds, **439**.
 Monoketones, 307.
 Mononitrobenzene, 471.
 Mononitroethane, 376.
 Mononitroparaffins, 376.
 Mononitrophenols, 472.
 Monophenyl sulfate, 470.
 Monosaccharids, 309.
 Monoses, 309.
 Monsel' salt, 201.
 Monureids, 406.
 Morphin, 369, **562**, 565, 566, 567.
 diacetyl, 369.
 Morphium, 547.
 sulfate, 378, **546**, 563.
 Morpholin, 520.
 Morrhuin, 367.
 Motion, 4.
 Mucedin 587.
 Mucilages, 321.
 Mucins, 583, 594.
 Mucoid., 583.
 Mucor, 600 602.
 Murexid 526, **527**.
 Muscarin, **383**, 385, 581.
 Muscle plasma, 585.
 serum, 585.
 stroma, 585.
 tissue, 585.
 Mustard oils, 380, 397.
 Myazin compounds, **522**.
 Mydalein, 386.
 Mydin, 476.
 Myogen, 582, 585.
 fibrin, 585.
 soluble, 585.
 Myosin, 582, 585.
 fibrin 585.
 Myrcene, 426.
 Myrosin, **432**, 465, 467, 606.

 Napellin, 568.
 Naphtha, 276.
 Naphthalene, 457, 493, **494**, 497.
 halids, 497.
 homologues, 495.
 phenanthrene, 494.
 sulfochlorid, 480, 500.
 sulfoglycin, 757.
 Naphthalinolin, 544.
 Naphthenes, 486.
 Naphthol blue, 520.
 yellow, 498.

 Naphthols, 439, 495, **497**, 498, 501.
 substituted, 498.
 Naphthoquinones, 495, 499.
 Naphthylamins, 498, 499, **500**, 538.
 Naphthylenes, 486.
 Narcein, 548, 562, **564**, 565, 566.
 Narcotin, 462, 463, **548**, 562, **464**, 565, 566.
 Nascent state, 168.
 Negative plate, 40.
 pole, 41.
 Neodymium, 55, 102, 103.
 Neon, 55, 101, 103, 125.
 Neuridin, 386.
 Neurin, **384** 385, 581.
 Neurokeratin, 595.
 Nickel, 249.
 sulfate, 249.
 Nicotidin 545.
 Nicotin, 518, 545, 548, **551**.
 Nile blue, 520.
 Niobium, 55, 101, 191.
 Nitranilins, 475.
 Nitrates, 118.
 Nitre, 223.
 Nitril bases, 377.
 Nitril, lactic, 398.
 Nitrils, 301, 328, 379, 388, 391, **393**, 394.
 395, 400, 410.
 aromatic, 456, 469.
 of carbonic acids, 395.
 of dicarboxylic acids, 394.
 of fatty acids, 393.
 of ketone acids, 393, **398**.
 of oxyacids, 300, **397**.
 of thiocarbonic acids, 395.
 Nitrites, 156.
 Nitro, 376.
 acetophenone, **455**.
 acids, 410.
 alcohols, 408.
 aldehydes, 408.
 anisols, 472.
 benzenes, 440, **471**, 473, 474.
 benzole, 471.
 cresols, 472.
 diphenyls, 502.
 Nitrogen, 148.
 acids of, 156.
 amid, 377, 379, 380.
 amino, 580.
 azo, 377.
 basic, 580.
 bromid, 153.
 chlorid, 153.
 diamido, 580.
 dioxid, 154.
 group, 148.
 halids, 153.
 humus, 580.
 hydrazo, 377.
 imid, 377.
 monamido, 580.
 monoxid, 153.
 nitril, 377, 379, **380**.
 oxids of, 153.
 pentoxid, 156.
 peroxid, 155.
 primary, 377.
 protoxid, 153.
 secondary, 377.
 tertiary, 377.
 tetroxid, 377.

- Nitroso group, 350.
- Nitrosonaphthols, 498.
- Nitrosophenols, 472.
- Nitrosyl bichlorid, 158.
- chlorid, 158, 413, 487.
- Nitrotoluenes, 471.
- Nitrouracil, 529.
- Nitrous fumes, 155.
- oxid, 153.
- Nitroxanthin, 534.
- Nomenclature, 80, 771.
- of alcohols, 285.
- of amins, 378.
- of carbon compounds, 271.
- Non-metals, 101.
- Nonoses, 307, 310.
- Normal conditions, 9, 24.
- gas, 10.
- volume, 24.
- Nortropan, 552.
- Nubecula, 731, 740.
- Nuclein bases, 531.
- Nucleins, 591, **592**, 619.
- Nucleoalbumins, 582, **586**.
- Nucleohiston, 583, 588, **591**, 666, 669.
- Nucleoproteids, 583, **591**, 592, 593, 631, 712.
- 721, 724.
- Occlusion, 107.
- Octoses, 309, 310, 600.
- Enoxidase, 606.
- Ohm, 46.
- Oil, bone, 517.
- cod-liver, 367.
- mustard, 432.
- of bitter almonds, 392, 453, 454.
- of Dippel, 510, 517, 518.
- of turpentine, 492.
- of vitriol, 144.
- sperm, 367.
- Oils, drying, 366.
- essential, 425, 428, 486, 488.
- fixed, 366.
- greasy, 366.
- lubricating, 276.
- mustard, 380, 397.
- neutral, 366.
- semidrying, 366.
- volatile, 366, 486, 488.
- Olefiant gas, 423.
- Orino acids, 101.
- compounds, 437.
- diazin, 520, 521.
- dioxybenzene, 448.
- oxycarbinol, 475.
- toluenesulfoamid, 470.
- triazin, 436.
- Osazones, 299, 311, 316, 319, **484**, **485**.
- Osmium, 192.
- Osmosis, 18.
- Osmotic equivalent, 18.
- pressure, 66.
- of blood, 657, 658.
- Ossein, 596.
- Otoliths, 238.
- Ovialbumins, 582, **584**.
- Ovoglobulins, 582, **584**.
- Ovimucoid, 584.
- Ovittellin, 586.
- Oxacids, 64.
- Oxalylurea, 408, **515**, 527, 535.
- Oxamid, 401, 407.
- Oxazins, 520.
- Oxethylamin, 408.
- Oxhydri, 64.
- Oxidases, 606.
- Oxidation, 111.
- Oxide, 111.
- alkylen, 382.
- basic, 112.
- indifferent, 112.
- neutral, 112.
- saline, 112.
- Oxim group, 388.
- Oximid, 401.
- Oximidoacetone, 398.
- Oxims, 299, 452, 499.
- Oxindole, 478, 539, **541**.
- Oxyacids, 64, 300, **338**, 362, 398, 413.
- Oxyaldehyde ketones, 308.
- Oxyaldehydes, 300, **308**, 309, 335, **339**.
- Oxyamids, 411.
- Oxyamins, **382**, 385, 408.
- Oxyanthracenes, 499.
- Oxyazo compounds, 482.
- Oxybenzaldehyde, 454.
- Oxycholin, 384.
- Oxycinchonin, 558.
- Oxycyanids, 300, **337**, **339**.
- Oxydimorphin, 563.

- Oxymorphan**, 563.
Oxynaphthalenes, 497.
Oxynaphthylamin, 501.
Oxyneurin, 384.
Oxyphenylethylamin, 476, 479, 617, 631.
Oxypiperidins, 413.
Oxypurins 531, 532, 533.
Oxypyrimidins, 523.
Oxyquinolins, 544.
Oxysalts, 66.
Oxyuracils, 529.
Ozocerite, 374.
Ozone, 112.
- Palladium**, 213.
Pancreatic diabetes, 683, 746.
 diastase, 643.
 digestion, 625.
 secretion, 625, 626.
Papaveraldin, 565.
Papaverin, 548, 562, 564, 565, 566.
Papayotin, 606.
Para acetanisidin, 477.
 acetophenetidin, 477.
Paralbumin, 595.
Para amidoazobenzene, 483.
 amidodiphenyl, 439, 502.
 amidophenol, 475.
 amidophenylalanin, 479.
 amidothiazin, 520.
 amidotriphenylmethane, 504.
 azoamido compounds, 482.
 compounds, 437.
 coniin, 550.
 cresol, 646, 647.
 diamidodiphenyl, 484.
 diamidotriphenylmethane, 505.
 diazin, 520, 521, 522.
 dioxybenzene, 449.
 euglobulin, 653.
Paraffin, 276.
 series, 273.
Paraffus, 273.
 amido, 377.
 diamido, 387.
 dihalogen, 277.
 dinitro, 385.
 halid, 277.
 imido, 377.
 monohalogen, 277.
 nitro, 376.
 nitrogen derivatives of, 376.
 oxidation products of, 282.
 sulfur derivatives of, 370.
Para formaldehyde, 301.
 globulin, 652.
 histon, 588.
Paraldehyde, 303.
Paramorphin, 565.
Paramylum, 321.
Para nitrophenylalanin, 479.
 nitrosophenol, 473.
 nucleins, 586.
 oxyphenylalanin, 478.
 phenetidin, 477.
 phenylenediamin, 484.
 pseudoglobulin, 653.
 rosanilin, 503.
 tetramethyldiamidotriphenylmethane, 505.
 thioformaldehyde, 373.
 triazins, 394, 536, 537.
- Para xanthin**, 532, 533, 724.
 xylene, 442.
Parchment paper, 322.
Paris green, 176, 252.
Parvolins, 518.
Pearl ash, 225.
Pear oil, 363.
Pelletierin, 548, 549.
Penicillium, 342, 601, 602.
Pentabromanilin, 475.
Pentamethylenediamin, 386, 418, 519.
Pentane, 518.
Pentapeptids, 416.
Pentene, 425.
Pentites, 297.
Pentole, 507.
Pentosanes, 311.
Pentoses, 298, 309, 310, 323, 326, 465, 509, 593, 600, 753.
Pentosids, 465.
Pentosuria, 753.
Pepsin, 590, 603, 610, 620, 624, 645.
Pepsinogen, 610, 611, 624.
Peptoids, 616, 617, 618, 629.
Peptomelanin, 615.
Peptone plasma, 650.
 urinary, 739.
Peptones, 583, 614, 616, 617, 618, 625, 628, 629, 630, 645.
Peptonuria, 739.
Periodic law, 102, 104.
Perissads, 59.
Permanganates, 196.
Peroxids, 352.
Petroleum, 276.
 ether, 276.
Pfeiffer's phenomenon, 672.
Phagocytosis, 670.
Phallin, 573.
Phase rule, 93.
Phases, 93.
Phellandrin, 488.
Phenacetin, 477.
Phenanthrene, 493, 495, 497, 501.
 alkaloids, 548, 562, 565.
 quinolin, 563.
Phenanthridin, 538.
Phenanthrolins, 545.
Phenanthroquinone, 496.
Phenates, 446, 464.
Phenazone, 521.
Phenetidins, 472, 477.
Phenetol, 464.
Phenol, 444, 470, 472, 581, 646, 647.
 aldehydes, 458.
 allyl, 450.
 cymlic, 447.
 dyes, 450.
 esters, 446.
 phthalein, 451.
 propenyl, 450.
Phenols, 443, 469, 481, 482, 491.
 benzyllic, 446.
 cresylic, 446.
 dihydric, 448.
 diphenyl, 502.
 methylisopropyl, 447.
 monohydric, 444.
 naphthalene, 497.
 substituted, 447.
 trihydric, 449.
 unsaturated, 450.

- Phenones, 455.
 Phenyl, 443, 446.
 acetaldehyde, 479.
 acetamid, 475.
 acetylene, 442, 458.
 acrolein, 454.
 alanin, 416, 473, 479, 595, 596, 614, 617, 703.
 alkylhydrasins, 484.
 amins, 473, 476.
 benzenes, 501.
 carbamin, 476.
 cyanidins, 537.
 dimethylpyrazolon, 513.
 Phenylene, 443.
 diamins, 476.
 Phenyl esters, 446.
 ethene, 442.
 ether, 464.
 ethylamin, 582.
 glucosid, 465.
 glycocoll, 473, 479, 539, 542.
 guanidin, 480.
 hydrasids, 343.
 hydrasin, 299, 325, 390, 405, 410, 484, 486, 513.
 hydrazones, 434, 485, 486, 540.
 hydroxid, 444.
 hydroxylamin, 473.
 iodid, 444.
 isocyanid, 394, 476.
 methylpyrazoles, 513.
 phosphates, 444.
 phosphoric tetrachlorid, 444.
 pyridins, 519.
 pyridyle, 545.
 salicylate, 459.
 semicarbasid, 405.
 sulfid, 469.
 sulfochlorid, 480.
 uracil, 525.
 urea, 480.
 urethans, 402, 480.
 Phlebin, 659.
 Phloretin, 467.
 Phloridzin, 467.
 diabetes, 682, 744.
 Phloroglucin, 449, 467.
 Phloroglucite, 489.
 Phlorose, 467.
 Phorone, 428.
 Phosgene, 304, 352, 353.
 Phosphamin, 165.
 Phosphates, 167.
 Phosphin, 165.
 Phosphins, 422.
 Phosphoglobulins, 586.
 Phosphoglycoproteids, 583.
 Phosphonia, 165.
 Phosphorus 148, 159.
 acids of, 166.
 analysis of, 162.
 bromids, 165.
 fluorids, 165.
 halids, 165, 277, 352.
 iodids, 165.
 organic compounds of, 422.
 oxids, 166.
 oxychlorid, 165.
 pentachlorid, 165, 299, 300, 443, 463, 469.
 pentoxid, 166.
 trichlorid, 165.
 Phosphorus trioxid, 166.
 Phthalamid, 477.
 Phthalefins, 444, 461, 468, 504.
 Phthalid, 462.
 Phthalids, 504.
 Phthalimid, 417, 477.
 Phycite, 297.
 Physostigmin, 570.
 Phytoglobulin, 586.
 Phytovitellin, 582, 586.
 Picene, 493, 494, 495.
 Picolins, 518, 519, 550.
 Pieramid, 475.
 Pilocarpene, 556.
 Pilocarpidin, 556.
 Pilocarpin, 519, 548, 549, 556.
 Pimelin ketone, 491.
 Pinene, 483, 490.
 dibromo, 488.
 hydrochlorid, 488.
 Piperasin, 387, 523.
 urate, 531.
 Piperidein, 519.
 alkaloids, 548, 549.
 Piperidin, 301, 387, 508, 516, 518, 519, 550.
 alkaloids, 548, 549.
 Piperidins, 517, 519.
 Piperidium chlorid, 378.
 Piperin, 458, 519, 548, 550.
 Pitch, 440.
 Plaques, 656, 667.
 Plasma, 649, 650.
 oxalate, 650.
 peptone, 650.
 salt, 650.
 salts of, 655.
 Plastens, 629.
 Plaster of Paris, 237.
 Platinic chlorid, 214.
 Platinocyanids, 399.
 Platinum, 213, 214.
 black, 214.
 colloidal, 604.
 group, 213.
 spongy, 214.
 Plumbago, 188.
 Plumbates, 205.
 Plumbites, 205.
 Pæonin, 450.
 Poisons, 132.
 mineral, 182.
 Polarimetry, 37.
 Polarization, electric, 44.
 Poles, electric, 40.
 Polymerization, 301, 433.
 Polymethylenes, 434.
 Polypeptids, 415, 522, 578, 579, 581, 617, 629, 630.
 Polysaccharids, 309, 311, 319, 644.
 Polyuria, 695.
 Pompholix, 243.
 Ponceau, 496.
 Populin, 468.
 Porcelain, 248.
 Porter, 290.
 Positive plate, 40.
 pole, 41.
 Potash, 215, 222, 225.
 Potassa, 222.
 Potassium, 215, 222.
 acetate, 225.
 aluminate, 247.

- Potassium arsenite**, 175.
 bromate, 223.
 bromid, 223.
 carbonates, 225.
 chlorate, 224.
 chlorid, 223.
 cyanid, 228.
 dichromate, 224.
 disulfid, 223.
 ethylsulfate, 393.
 ferricyanid, 229.
 ferrocyanid, 228, 353.
 hypochlorite, 224.
 hydroxid, 222.
 iodhydrargyrate, 548.
 iodid, 223.
 monosulfid, 223.
 myronate, 432.
 nitrate, 223.
 oxalates, 226.
 oxids, 222.
 pentasulfid, 223.
 permanganate, 225.
 phenate, 444, 446, 465, 470.
 pyrogallate, 450.
 sulfates, 224.
 sulfhydrate, 223.
 sulfids, 223.
 sulfites, 224.
 tartrates, 226.
 thiocyanate, 607.
 trisulfid, 223.
 urates, 531.
Potential difference, 41.
 fall of, 43.
 gradient, 43.
Pouchet's base, 733.
Powder of Algaroth, 184.
Power, 8, 46.
Praseodymium, 55, 102, 103.
Precipitation limits, 576, 577.
Precipitins, 670, 672, 675.
Pressure, 10, 30.
 critical, 29, 30.
 osmotic, 66.
 partial, 20.
 solution, 70.
 standard, 24.
Process (see also **Reagent**, **Reaction**, **Test**).
 Babcock's, 765.
 Fehling's, 751, 752.
 Fischer and Bergell's, 757.
 Focke's, 750.
 Freund and Lieblein's, 698.
 Hammerschlag's, 675.
 Knapp's, 750.
 Külz's, 756.
 Löwy's, 676.
 Martius and Lüttke's, 622.
 Mohr's, 701.
 Mörner and Sjöqvist's, 622.
 Panum's, 736, 739.
 Rittenhausen's, 766.
 Robert's, 752.
 Sharples', 765.
 Volhard's, 701.
Proenzymes, 604.
Prolin, 416, 511, 763.
Propaldehyde, 305.
Propantriol, 295, 296.
Propargyl halids, 426.
Propenyl anisol, 450.
Propenyl phenol, 450.
Propepsin, 611.
Propeptones, 582.
Propidene phenylhydrazin, 541.
Propyl amin, 382.
 benzene, 441.
 carbinol, 292.
 hydroxid, 291.
 piperidin, 519, 550.
 pseudonitrol, 376.
 pyridins, 518.
Prosecretin, 626.
Protamin nucleates, 591.
Protamins, 417, 580, 582, 587, 588, 630.
Protelds, 583, 591, 619, 630.
Proteinochrome, 540.
Proteinochromogen, 540.
Proteins, 575, 643, 645, 646, 733.
 classification of, 582.
 color reactions of, 577.
 decompositions of, 579.
Proteoses, 612.
Prothrombin, 652, 654, 666, 668.
Protoalbumoses, 613, 614, 618.
Protoelastose, 596.
Protones, 589.
Prussian blue, 203, 229.
Pseudo aconitin, 569.
 conhydrin, 549.
 globulin, 652.
 hæmoglobin, 662.
 morphin, 563.
 mucin, 594.
 nitrols, 376.
 nucleins, 586.
 pelletierin, 548, 549.
 pepsin, 609, 611.
 urea, 389, 406.
Psychrometer, 150.
Ptomains, 383, 385, 476, 518, 519, 570, 582.
Ptyalin, 607, 619, 631, 642.
Pulegone, 491.
Purin, 528.
 bases, 531.
 compounds, 522.
 group, 522, 527.
Purpurin, 500.
Pus, 693.
Putrefaction, 581, 646.
Putrescin, 388, 417, 581, 617, 758.
Pyoktanins, 506.
Pyrazin, 516, 520, 521.
Pyrazoles, 512, 514.
Pyrazolin, 512.
Pyrazolons, 512.
Pyridiazin, 520, 521.
Pyridin, 301, 433, 507, 508, 509, 516, 518, 523, 545.
 alkaloids, 548.
 bases, 510, 517, 558.
 homologues, 518.
Pyridylpyrrole, 545.
Pyrimidin, 520, 521, 523.
 derivatives, 522.
Pyrites, 138, 144, 169, 197, 199.
 copper, 250.
Pyrocatechin, 448.
Pyrocatechol, 447, 448, 647.
Pyrocomane, 516.
Pyrodin, 486.
Pyrogallol, 450, 461, 467.
Pyrolusite, 195, 196.

- Pyrone, 516, 517.
 Pyroxam, 321.
 Pyroxylin, 323.
 soluble, 323.
 Pyrroles, 511.
 Pyrrole, 507, 508, 509, 510, 512, 517, 664.
 Pyrrolidin, 511.
 alkaloids, 548.
 piperidin alkaloids, 548, 552.
 pyridin alkaloids, 548, 551.
 Pyrrolidone, 511.
 Pyrrolin, 511.
 Pyrromonazoles, 513, 514.
- Quarternary ammonium compounds, 379,
 382, 383, 384.
 hydroxids, 377.
- Quercite, 489.
 Quicklime, 235.
 Quina red, 462.
 Quinidin, 558.
 Quinidin, 556, 558.
 Quinin, 519, 543, 556, 559.
 hydrosulfate, 557.
 sulfate, 557.
- Quinite, 489.
 Quinol, 447, 449, 729.
 Quinolin, 474, 478, 507, 519, 538, 543, 558.
 alkaloids, 548, 556.
 bases, 543.
 homologues, 544.
- Quinone, 449, 450, 452.
 dioxim, 452.
- Quinones, 451, 472, 499.
 Quinoxim, 473.
- Radicals, 84, 263.
 Radium, 55, 102, 103.
 Raffinose, 319, 602.
- Reaction, 61 (see Process, Reagent, Test).
 velocity of, 90.
- Reactions, endothermic, 97.
 exothermic, 97.
 reversible, 89.
- Reagent, Blum's, 738.
 Boas', 621.
 DeVries', 548.
 Esbach's, 738.
 Fröhde's, 563.
 Gunzburg's, 621.
 Krüger-Wolff, 530.
 Marquis', 564.
 Mayer's, 548.
 Millon's, 578.
 Nessler's, 151.
 Oliver's, 737.
 Riegler's, 737.
 Roberts', 736.
 Roch's, 737.
 Schiff's, 326, 506.
 Sonnenschein's, 548.
 Spiegler's, 737.
 Stokes, 659.
 Stryzowski's, 664.
 Tanret's, 737.
 Töpfer's, 621.
 Uffelmann's, 623.
- Realgar, 174.
 Reaumur's scale, 22.
 Receptors, 673, 674, 675.
 Reduction, 108.
 Refraction, index of, 34.
- Rennin, 617.
 Residues, 84.
 Resins, 493.
 Resistance, 42, 45.
 Resistivity, 42.
 Resorcinol, 447, 448, 457.
 phthalein, 451.
- Respiration, 686.
 changes of air in, 686.
 tissue, 691.
- Respiratory quotient, 687.
 Reticulin, 583, 597.
- Reversible reactions, 89.
- Rhamnose, 311.
- Rhigolene, 276.
- Rhodinol, 427.
- Rhodium, 213.
- Ribose, 311.
- Ricin, 572.
- Roburite, 471.
- Rochelle salt, 227.
- Rosanilins, 474, 476, 503, 505.
- Rosin, 488.
- Rouge, 198.
- Rubidium, 215, 230.
- Ruby, 246.
- Rufol, 499.
- Ruthenium, 213.
- Sabadillin, 570.
- Saccharates, 311, 315, 318.
- Saccharin, 470.
- Saccharobioses, 309, 316.
- Saccharomyces, 326, 327, 600, 602, 603.
- Saccharose, 316, 600, 602, 643, 644, 681.
- Saccharotrioses, 309.
- Saffranins, 520.
- Saffrol, 450.
- Sal ammoniac, 233.
- Salacetol, 459.
- Salæratum, 226.
- Salicin, 453, 454, 459, 467.
- Salicyl hydrid, 454.
- Salicylal, 454.
- Saligenin, 453, 468.
- Salipyrin, 514.
- Saliva, 606.
- Salmin, 589.
- Salmon, 588.
- Salol, 444, 469, 625.
- Salt, 217.
 of Saturn, 206.
 of sorrel, 226.
 rock, 217.
- Salting out, 576.
- Saltpeter, 223.
- Chile, 218.
- cubic, 218.
- Salts, 63, 65.
 acid, 66, 83.
 basic, 66, 83.
 double, 83.
 haloid, 66.
- Samarium, 55, 102, 103.
- Sandarach, 174.
- Saponification, 359.
- Sapphire, 246.
- Saprins, 386.
- Sarcosin, 390, 403, 414, 515.
- Sarkin, 533.
- Saturated compounds, 273.
- Scandium, 55, 102, 103, 245.

- Scheele's green, 252.
 Schweinfurth green, 252.
 Scobron, 588, 589.
 Scopolamin, 553, 555.
 Secalia, 381.
 Secretin, 626.
 Seidlitz salt, 241.
 Selenazoles, 511.
 Selenite, 237.
 Selenium, 147.
 Selenmonazole, 512.
 Sericin, 420, 597.
 Series, electrochemical, 62.
 Serin, 430, 579, 580, 595.
 Serines, 653.
 Serum albumin, 582, 653, 733.
 carbohydrates of, 654.
 fats of, 654.
 globulin, 582, 653, 733, 738.
 salts of, 655.
 Siemens' unit, 46.
 Silix, 191.
 Silicates, 191.
 Silicibromoform, 191.
 Silicichloroform, 191.
 Silicium, 190.
 Silicon, 188, 190.
 carbide, 161.
 chloride, 191.
 Silver, 215, 330.
 acetyl, 425.
 bromide, 231.
 chloride, 231.
 cyanide, 231.
 fulminate, 396.
 german, 249.
 monoxide, 231.
 nitrate, 231.
 oxalate, 301.
 oxide, 230.
 thiocyanate, 432.
 Sincalin, 383.
 Skatole, 540, 541, 579, 580, 581, 597, 614, 646.
 Skatosin, 617, 631.
 Skatoxyl, 646.
 Soaps, 429.
 Soapstone, 240.
 Soda, 220.
 baking, 221, 227.
 caustic, 217.
 washing, 220.
 Sodium, 215, 216.
 acetate, 220.
 acetanilide, 476.
 acetyl, 425.
 aluminate, 247.
 arsenates, 219.
 arsenites, 175, 219.
 benzoylacetate, 523.
 bicarbonate, 221.
 borate, 219.
 bromide, 217.
 carbonates, 220.
 chlorate, 220.
 chloride, 217, 576.
 dioxide, 216.
 ethylate, 361, 532.
 ethylthiosulfate, 373.
 glycocholate, 636.
 group, 215.
 Sodium, hydroxide, 217.
 hypochlorite, 220.
 hyposulfite, 218.
 iodide, 217.
 manganate, 220.
 metaphosphate, 219.
 methyl, 329.
 monoxide, 216.
 nitrate, 218.
 nitroprusside, 399.
 oxide, 216.
 phenate, 458, 459.
 phenylhydrazine, 484.
 phenylsulfide, 444.
 phosphates, 219.
 pyroborate, 219.
 pyrophosphate, 219.
 sesquicarbonate, 221.
 silicates, 218.
 sulfates, 218, 576.
 sulfite, 218.
 taurocholate, 636.
 thiosulfate, 218.
 tungstate, 192.
 urates, 531.
 Solanidin, 468.
 Solanin, 468.
 Solute, 27.
 Solution—Solutions, 27.
 dilute, 28.
 heat of, 98.
 ideal, 28.
 normal, 65.
 pressure, 70.
 saturated, 28.
 solid, 51.
 supersaturated, 28.
 standard, 65.
 Solubilities, 776.
 Solvay process, 221.
 Solvent, 27.
 Somnal, 402.
 Sorbinose, 311, 315.
 Sorbite, 298.
 Sorbitol, 298.
 Space isomerism, 311.
 Spasmodic, 572.
 Specific conductance, 41.
 heat, 33.
 resistance, 41.
 rotary power, 38.
 volume, 10.
 weight, 10.
 Spectroscopy, 34, 35.
 Spermaceti, 363.
 Spermin, 387.
 Spirit, methylated, 287.
 potatoe, 292.
 pyroacetic, 307.
 pyroxylic, 286, 329.
 Spirits, 288, 291.
 Spongin, 583, 597.
 Stable substances, 87.
 Stannates, 212.
 Stannic chloride, 213.
 oxide, 212.
 Stannous chloride, 212.
 oxide, 212.
 Starch, 287, 319, 330, 642, 644.
 animal, 321.
 cellulose, 321.
 hydrated, 320.

- Starch, iodid, 321.
 paste, 320.
 soluble, 321, 322.
 States of matter, 12.
 Stearoptenes, 488.
 Steapsin, 627, 631.
 Steel, 197.
 Stercobilin, 637, 642, 648.
 Stercorin, 642.
 Stereochemistry, 312.
 Stereoisomerism, 311, 600, 673.
 Stethol, 363.
 Stibamin, 183.
 Stibins, 422.
 Stibonia, 183.
 Stilbene, 502, 503.
 Stoiichiometry, 78.
 Stomach contents, 620.
 function of, 609.
 Strength, 75.
 Strontianite, 238.
 Strontium, 235, 339.
 Strychnidin, 560.
 Strychnin, 559.
 Strychnos alkaloids, 548, 559.
 Sturin, 589.
 Styracol, 448.
 Styrolene, 442.
 Suberone, 552.
 Sublimate, corrosive, 257.
 Sublimation, 32.
 Substitution, 269.
 Succinimid, 403, 408.
 Succus entericus, 632.
 pyloricus, 608.
 Sucrase, 602, 632.
 Sucrates, 318.
 Sugar, beet, 316 317.
 burnt, 317.
 candy, 317.
 cane, 316.
 diabetic, 314.
 fruit, 315.
 gelatin, 413.
 grape, 314.
 liver, 314.
 maple, 316, 317.
 milk, 318.
 of lead, 206.
 invert, 316.
 raw, 317.
 Sulfates, 146.
 Sulfethylates, 359.
 Sulfids, 141, 371.
 Sulfites, 144.
 Sulfocarbulates, 470.
 Sulfochlorids, 469.
 Sulfonal, 374, 641.
 Sulfonation, 469.
 Sulfones, 370, 372, 469.
 of mercaptols, 373.
 of thioaldehydes, 372.
 Sulfuryl chlorid, 143.
 Sulfovinates, 359.
 Sulfoxids, 370, 372.
 Sulfur, 38.
 bromid, 142.
 chlorid, 142.
 dioxid, 142.
 flowers of, 138.
 group, 138.
 iodid, 142.
 loosely combined, 590.
 oxids, 143.
 precipitated, 138.
 roll, 138.
 ruby, 174.
 trioxid, 143.
 Sulfureids, 474.
 Sultones, 498.
 Superfusion, 29.
 Superphosphate, 237.
 Sylvestrene, 488.
 Symbols, 60.
 Synalbumose, 614.
 Synthesis, 62, 115, 262, 599.
 Syntonin, 590, 624.
 Talc, 240.
 Talose, 311.
 Tanacetone, 491.
 Tannins, 461.
 Tantalum, 55, 101, 103, 191, 193.
 Tartar, cream of, 345.
 crude, 226.
 emetic, 237.
 salt of, 226.
 Tartronylurea, 527.
 Tata-albumen, 584, 590.
 Taurin, 372, 421, 422, 432, 634, 636, 639,
 640, 680, 730.
 Taurocyanamin, 421.
 Tauroglycoecyanamin, 421.
 Teichmann's crystals, 664.
 Tellurium, 147.
 Temperature, 21.
 absolute, 24.
 critical, 29, 30.
 standard, 24.
 Tension, 30.
 Terbium, 55, 102, 103.
 Terpens, 487.
 Terpene nitroschlorid, 487.
 Terpenes, 466.
 Terpin, 488.
 hydrate, 490, 491.
 Terpinene, 488.
 Terpineols, 488.
 Terpinogens, 425.
 Terpinolene, 487.
 Terpins, 490.
 Terra alba, 237.
 Test, (Process, Reaction)
 Adamkiewicz, 540, 578, 588, 592, 596,
 613.
 Almén, 325.
 Arnold, 755.
 Baeyer, 325.
 Barfoed, 324.
 Baumann, 323.
 Berg, 326.
 biuret, 407, 416, 578, 586, 587, 588, 589,
 592, 596, 613, 615, 616, 617, 627, 628,
 629, 630.
 Boettger, 325.
 Conradi, 326.
 Denigès, 479.
 Ehrlich, 743.
 Ewald, 625.
 Fehling, 324, 749.
 fermentation, 326, 749.
 ferrocyanid, 736.
 Fischer, 325.
 Fresenius, & von Babo, 182.

- Test, furfurole, 635.
 Gallois, 489.
 Gerhardt, 755.
 Gmelin, 637, 649, 742.
 Gmelin-Rosenbach, 742.
 guaiac, 741.
 Hammarsten, 637, 742.
 heat and nitric acid, 73^f
 Heller, 735, 741, 743.
 Hoffman, 479.
 Hofmeister, 415.
 Hoppe-Seyler, 325.
 Huppert, 637.
 Husemann, 564.
 indophenol, 475, 477.
 Jaffé, 544.
 Knapp, 325.
 Kossel, 534, 536.
 Legal, 755.
 Lieben, 755.
 Lieben-Gunning, 755.
 Liebermann, 578.
 Marsh, 180.
 Millon, 578, 586, 588, 589, 592, 595, 596, 615, 616, 617.
 Molisch, 323, 579, 581, 613, 614, 615, 616, 617.
 Mulder-Neubauer, 325, 542.
 murexid, 530, 639.
 Nessler, 151, 623.
 Neumann-Wender, 325.
 Nylander, 325, 749.
 Obermüller, 639.
 Pavy, 756.
 Pellagri, 564.
 Penzold, 756.
 Pettenkofer, 323, 510, 635, 649, 742.
 phenylhydrazin, 325, 485, 750.
 phloroglucin-vanillin, 621.
 pine-shaving, 445, 466, 509, 510, 540, 543.
 Piria, 479.
 precipitin, 672.
 Quirini, 325.
 Reinsch, 178.
 resorcin-sugar, 621.
 Reynold, 756.
 Riegler, 325.
 Rosenbach, 730.
 Salkowski, 639.
 Scherer, 415, 479, 489.
 Schiff, 323, 509, 639.
 Seliwnaoff, 326, 749.
 Smith, 743.
 Tiechmann, 741.
 Tollens, 323, 593.
 Töpfer, 622.
 trichloroacetic acid, 737.
 Trommer, 324.
 Villiers-Fayolle, 326.
 Vitali, 554.
 Vogel, 325.
 Wiedel, 516, 524, 525, 527, 533, 534, 535, 536.
 Widal, 672.
 xanthin, 533, 535.
 xanthoproteic, 578, 588, 592, 595, 596, 613, 615.
 Tetanin, 572.
 Tetanotoxin, 572.
 Tetra bromanilin, 475.
 glycylglycin, 416.
 Tetra hydrobenzenes, 434, 486.
 hydrodiphenyl, 502.
 hydroglyoxalin, 514.
 hydronaphthols, 498.
 hydronaphthylamin, 501.
 hypopyridins, 519.
 hypopyrimidins, 523.
 hypopyrrole, 511.
 hydroquinolins, 544.
 hydrostrychnin, 560.
 ketohexahypopyrimidin, 527.
 ketones, 308.
 methylammonium hydroxid, 381.
 methylbenzenes, 441.
 methyldiamidodiphenylmethane, 503.
 methylenediamin, 386, 417, 511.
 methyleneimin, 511.
 Tetrammonium iodids, 379.
 Tetronal, 374.
 Tetrapeptids, 416.
 Tetraphenylpyrimidins, 545.
 Tetraphenylsilicon, 502.
 Tetrazin, 508.
 Tetrazoles, 511, 512.
 Tetrethylammonium hydroxid, 382.
 Tetriodopyrrole, 511.
 Tetroses, 309, 310.
 Thallin, 544.
 Thallium, 55, 102, 103, 235.
 Thebain, 562, 565, 567.
 Thebaol, 567.
 Thein, 533.
 Theobromin, 533, 546.
 Theophyllin, 532, 533.
 Theory, atomic, 52.
 Ehrlich's 672.
 molecular, 52.
 side-chain, 673.
 Therm, 22.
 Thermal capacity, 23.
 unit, 22.
 Thermochemistry, 97.
 Thermolabile substances, 671.
 Thermometers, 21.
 Thermostable substances, 671.
 Thetin, 508.
 Thialdin, 303.
 Thiazins, 520.
 Thio acetals, 373.
 acids, 370, 374.
 albumose, 615, 618.
 alcohols, 370, 371, 372.
 aldehydes, 305, 370, 372.
 anhydrides, 141, 374.
 antimonates, 186.
 antimonites, 185.
 arsenates, 174.
 azoles, 511.
 bases, 64.
 Thiocol, 448.
 Thio cyanates, 397.
 ethers, 370, 371.
 ethylates, 372.
 glycols, 372.
 ketones, 370.
 monazoles, 612.
 Thionin, 520.
 Thionyl chlorid, 398.
 Thiophene, 507, 508, 509, 510.
 Thiophenol, 469.
 Thiourea, 405, 406.
 Thorium, 55, 102, 103.

- Thrombin, 661, 662, 663.
 Thrombosin, 669.
 Thujane, 491.
 Thulium, 55, 102, 103.
 Thymene, 447.
 Thymine, 523, 524, 525, 593.
 Thymol, 447.
 Tin, 211, 212.
 chloride, 212.
 crystals, 212.
 group, 211.
 hydrates, 212.
 oxide, 212.
 Tinstone, 212.
 Tinical, 219.
 Tinctures, 288.
 Titanium, 55, 102, 103.
 Tolane, 502, 503.
 Toluene, 441, 456, 469, 471.
 sulfonic chloride, 469.
 Toluidine, 472, 474.
 Toluol, 441.
 Toluyl benzene, 501.
 dimethylpyrazolon, 514.
 Toluylene, 503.
 Tolypyrin, 514.
 Topas, 245, 246.
 Toxalbumins, 572, 669, 672.
 Toxicology, acids, 132.
 aconite, 569.
 ammonia, 234.
 antimony, 186.
 arsenic, 175.
 atropin, 554.
 barium, 240.
 bismuth, 211.
 carbolic acid, 445.
 carbon dioxide, 355.
 carbon disulfide, 375.
 carbon monoxide, 353.
 chloral, 304.
 chloroform, 279.
 copper, 253.
 cyanide, 392.
 hydrogen sulfide, 140.
 illuminating gas, 353.
 lead, 207.
 mercury, 260.
 nicotin, 551.
 nitric acid, 159.
 nitrogen tetroxide, 155.
 opium, 567.
 oxalic acid, 336.
 phenol, 445.
 phosphorus, 161.
 potassium, 229.
 silver, 231.
 strychnin, 561.
 sulfuric acid, 147.
 zinc, 244.
 Toxins, 570, 572, 669, 673, 674.
 Toxophores, 673, 674.
 Transposition, 62.
 Transterpene, 490.
 Transudates, 692, 693.
 Triacetin, 296.
 Triacetamid, 409.
 Triamido azobenzene, 476.
 benzenes, 476.
 triphenylmethanes, 505.
 Triamids, 309.
 Triamins, 377, 389.
 Triasins, 536.
 Triasoles, 511, 512.
 Tribromhydrin, 338.
 Tribrommethane, 280.
 Tribromoanthraquinone, 502.
 Tribromophenol, 445.
 Tributyrin, 365.
 Tricaprin, 365.
 Tricaproin, 365.
 Tricaprylin, 365.
 Trichloro acetal, 303.
 acetylchloride, 303.
 aldehyde, 303.
 aniline, 475.
 butaldehyde, 303.
 methane, 278.
 Tricyanhydrin, 338.
 Tricyanogen chloride, 303, 537.
 Triformaldehyde, 373.
 Triformoxin, 410.
 Tryglyceride, 296.
 Trigonellin, 548, 549.
 Trilodometane, 280.
 Triketones, 303.
 Triketohexahydropyrimidin, 536, 537.
 Triketopurin, 528.
 Triketotetrahydroglyoxalin, 515.
 Trimargarin, 365.
 Trimethylamin, 381, 383, 384.
 Trimethylbenzenes, 441, 442.
 Trimethylethylene, 423.
 Trimethylene, 434.
 bromide, 434, 552.
 cyanide, 552.
 diamine, 386.
 imide, 508.
 oxide, 508.
 trisulfone, 373.
 Trimethylita, 381.
 Trimethyloxethylammonium hydroxide, 383.
 Trimethyloxethylideneammonium hydroxide, 383.
 Trimethyluracil, 524.
 Trimethylvinylammonium hydroxide, 384.
 Trimethylxanthin, 533.
 Trinitranilin, 475.
 Trinitrophenols, 442, 472.
 Triolein, 366.
 Triols, 295.
 Trional, 374.
 Trioses, 309, 310.
 Trioxanthraquinone, 500.
 Trioxycyanidin, 396, 537.
 Trioxymethylanthraquinone, 500.
 Trioxymethylene, 391.
 Tripalmitin, 365.
 Tripeptides, 416.
 Triphenylbenzene, 501.
 Triphenylethydrin, 537.
 Triple phosphate, 241, 705.
 point, 94.
 Trisaccharide, 309, 319.
 Tristearin, 365.
 Trithioacetaldehyde, 305.
 Trithioacetone, 373.
 Trithioformaldehyde, 373.
 Tropacocain, 548, 552.
 Tropan, 552, 553.
 alkaloids, 552.
 Tropeins, 553, 555.
 Tropeolins, 498.
 Tropidin, 552, 553, 555.

- Tropin, 519, 552, 553, 554, 555.
 atropate, 554.
 tropate, 553.
 Truxillins, 548, 552.
 Trypsin, 627, 628, 646.
 Trypsinogen, 627.
 Tryptophane, 540, 544, 578, 580, 581, 582, 589, 612, 614, 629, 632, 646.
 Tungsten, 192.
 Turnbull's blue, 203, 229.
 Turner's yellow, 206.
 Turpentine, 488.
 Tutty, 243.
 Tyrosin, 416, 478, 578, 579, 580, 581, 589, 595, 596, 606, 614, 617, 626, 631, 633, 646, 647, 757, 758, 763.

 Unit, Siemens', 46.
 Units, C. G. S., 46.
 fundamental, 7.
 Uracil, 523, 525, 593.
 bases, 592, 631.
 compounds, 522.
 group, 522, 523.
 Uralium, 402.
 Uranils, 526.
 Uranium, 203.
 Uranyl, 203.
 Urea, 389, 398, 403, 407, 408, 413, 418, 515, 523, 524, 526, 529, 530, 634, 655, 685, 686, 709, 710, 711, 712, 713, 714, 721.
 chlorids, 403, 403, 406, 477.
 nitrate, 405.
 oxalate, 405.
 Ureas, compound, 397, 406.
 Ureases, 606.
 Ureids, 406, 515.
 cyclic, 522.
 diacidyl, 407.
 mixed, 407.
 monacidyl, 406.
 Ureum nitrate, 378.
 Urethane, 402, 403.
 Urine, 694.
 abnormal constituents in, 733.
 pigments in, 743.
 acetone in, 753, 755.
 acetylacetic acid in, 753, 755.
 albumin in, 733.
 albumoses in, 736, 737, 738, 739.
 alkaline phosphates in, 704.
 allantoin in, 725.
 amido acids in, 756.
 ammonia in, 709, 710, 713, 753.
 biliary constituents in, 742.
 blood in, 741.
 chlorids in, 699, 700.
 chondroitin sulfates in, 740.
 chromogens of, 725.
 collection of samples of, 714.
 composition of, 699.
 concentration of, 698, 699.
 conjugate glucuronates in, 732, 750.
 consistency of, 694.
 creatin in, 720.
 creatinin in, 709, 710, 718, 719, 749.
 cryoscopy of, 698.
 cystin in, 757.
 diphenols in, 729.
 earthy phosphates in, 704.
 Ehrlich's diazo reaction of, 743.
 electric conductivity of, 699.
 Urine, endogenous uric acid in, 721.
 ester sulfates in, 702, 703, 728.
 exogenous uric acid in, 721.
 fermentation of, 601.
 freezing point of, 698.
 fructose in, 749, 752.
 glucose in, 744, 745, 749, 750 (see Glycosuria).
 glycocoll in, 756, 757.
 glycosurates in, 713.
 glyoxylic acid in, 713.
 hæmatoporphyrin in, 741.
 hæmoglobin in, 741.
 hippuric acid in, 724.
 histon in, 740.
 indican in, 729.
 indoxyl sulfates in, 729.
 inosite in, 753.
 lactose in, 752.
 lævulose in, 749, 752.
 lialose in, 752.
 leucin in, 757.
 maltose in, 749, 750, 752.
 metallic elements in, 706.
 mineral constituents of, 700.
 mucin in, 736, 740.
 neutral sulfur in, 702, 703, 727, 730.
 nitrogen distribution in, 706, 708, 709, 710.
 normal organic constituents of, 706.
 nucleoproteids in, 740.
 odor of, 696.
 osmotic pressure of, 698, 699.
 oxalates in, 731.
 oxaluric acid in, 725.
 oxybutyric acid in, 753, 754.
 pentoses in, 753.
 phenols in, 728.
 phosphates in, 703.
 physical characters of, 694.
 pigments of, 725.
 polarization of, 749, 750.
 proteins in, 733.
 quantitative determinations in, 713.
 of albumin, 738.
 of ammonia, 711.
 of chlorids, 701.
 of creatinin, 719.
 of earthy phosphates, 706.
 of ester sulfates, 702.
 of globulin, 738.
 of indican, 719.
 of mineral sulfur, 702.
 of oxalic acid, 711.
 of phosphates, 705.
 of total nitrogen, 707.
 of total sulfates, 702.
 of total sulfur, 702.
 of urea, 714.
 of uric acid, 723, 724.
 quantity of, 695.
 reaction of, 696.
 reducing substances in, 749.
 serum albumin in, 733, 734, 735, 736, 737.
 serum globulin in, 733, 734, 735, 736, 737, 738.
 skatoxylsulfates in, 730.
 specific gravity of, 695.
 sulfates in, 702, 703.
 sulfur in, 703, 727.
 thiocyanate in, 731.
 toxicity of, 733.

- Urine, tyrosin in, 757.
 undetermined nitrogen of, 708, 709, 710.
 urea in, 709, 710, 711, 714.
 uric acid in, 709, 910, 712, 720, 721, 722, 749.
 urobilinogen in, 725.
 urochrom in, 725.
 uroerythrin in, 725, 727.
 urohæmatin in, 730.
 uroxanthin in, 729.
 xanthin bases in, 712, 721, 724.
 Urinary mucoid, 740.
 Urobilin, 637, 642, 664, 665, 725, 726.
 Urobilinogen, 725, 726.
 Urobilinoids, 725.
 Urochrom, 725.
 Uroerythrin, 725, 727.
 Urohæmatin, 730.
 Urorosein, 743.
 Urostealiths, 759.
 Urotropin, 409.
 Uroxanthin, 541, 729.
- Valence, 59.
 Valerene, 425.
 Valerolactam, 413.
 Vanadium, 55, 101, 103, 191.
 Vanillin, 448, 454, 466.
 Vapor, 29, 30.
 pressure, 50.
 saturated, 31.
 tension, 31.
 unsaturated, 30, 49.
 Vaporization, 29.
 Vasech, 135.
 Vaseline, 277.
 Vegetable albumins, 584.
 globulins, 582, 584.
 Velocity, 4, 5.
 constant, 91.
 of reaction, 90.
 Veratrin, 579.
 Veratrol, 448, 449.
 Verdigris, 253.
 Vermilion, 256.
 antimony, 186.
 Veronal, 526.
 Verona yellow, 206.
 Vichy salt, 221.
 Vinegar, 320.
 wood, 329.
 Vinyl, 426.
 amin, 382, 384, 432.
 bromid, 424, 426.
 chlorid, 426.
 pyridin, 519.
 Vitellinoses, 613.
 Vitellins, 582.
 Vitriol, blue, 251.
 green, 200.
 oil of, 144.
 white, 244.
 Volt, 46.
 Volt, ampere 46.
 Voltage, 41.
 Voltameter, 45.
 Voltmeter, 46.
 Volume, specific, 10.
- Water, 113.
 baryta, 239.
 lime, 236.
- Water, maximum density of, 23, 50.
 of constitution, 115.
 of crystallization, 17, 113, 115.
 oxygenated, 123.
 soda, 354.
 Waters, natural, 116.
 chlorids in, 117.
 hardness of, 118.
 impurities in, 117.
 mineral, 121.
 organic matters in, 118.
 poisonous metals in, 119.
 purification of, 121.
 solids in, 117.
- Watt, 8, 46.
 Wax, 363.
 Weight, 5, 6.
 atomic, 54.
 equivalent, 60.
 molecular, 56, 267.
 specific, 10.
 Weights, 778.
 Whey, 617.
 albumin, 617.
 White of egg, 584.
 lead, 204, 207.
 precipitate, 258.
 Wines, 290.
 Witherite, 239.
 Witte's peptone, 613.
 Work, 8, 21, 46.
 Wort, 287.
- Xanthin, 530, 532, 533, 535.
 bases, 528, 530 531, 592, 712, 721, 724.
 Xanthocreatinin, 390.
 Xanthone, 459.
 Xanthoncs, 539.
 Xenols, 446.
 Xenon, 55, 101, 103, 125.
 Xylene, 459.
 glycols, 453.
 Xylenes, 441.
 Xylenols, 446.
 Xylidins, 474.
 Xylodin, 321.
 Xylols, 441.
 Xylose, 311, 593.
- Yeast, 600, 602,
 Yolk, 516.
 platelets, 586.
 Ytterbium, 55, 102, 103.
 Yttrium, 55, 102, 103.
- Zein, 587.
 Zinc, 240, 242, 634.
 alkyls, 307, 573.
 butter of, 243.
 chlorid, 243, 244.
 ethid, 375.
 ethyl, 375.
 hydroxid, 243.
 methid, 375.
 methyl, 375, 455.
 oxid, 243.
 sulfate, 244, 576.
 Zirconia, 211.
 Zirconium, 55, 102, 103, 211.
 Zymase, 602, 603.
 Zymogens, 604.
 Zymophores, 674.

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